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LXIII.—ON SODIC ZINCATES.

BY ARTHUR M. COMEY AND C. LORING JACKSON.

Although the solubility of zincic hydrate in alkalies is one of the most familiar facts in chemistry, very few attempts, so far as we can find, have been made to determine what compounds exist in such a solution. The reason for this is not far to seek, as the results obtained by the few who have studied this subject are so decidedly unsatisfactory that they are not likely to induce others to take up this line of work.

The first important papers in this field appeared in the *Annalen der Chemie und Pharmacie* in 1834, having been brought out by a prize offered from the Hagen-Bucholz foundation for work on zincic oxide. Of the various competitors, Laux,[1] who was most successful in his work on this part of the subject, found that a solution of zincic oxide in caustic alkali, if covered with a layer of alcohol, gradually deposited little shining crystals, which were easily soluble in water, and, he states, contained equal molecules of zincic oxide and the alkaline oxide (ZnO_2K_2). These crystals were decomposed by heat, giving a white powder, which contained one molecule of alkaline oxide to two of zincic oxide; but no analyses of either of these substances are given.

Two other competitors for this Hagen-Bucholz prize, Bonnet[2] and Sander,[3] also touch on this subject, but their results are of less

[1] Ann. Chem. (Liebig) **9**, 183. [2] Ibid. **9**, 177. [3] Ibid. **9**, 181.

importance. Sander, in fact, comes to the conclusion that no definite compound is formed when zincic oxide is dissolved in a caustic alkali.

The next paper on the subject was published in 1842, by Fremy,[1] who states that the compounds formed by zincic oxide and an alkali were in general deliquescent and amorphous, but by using a potassic hydrate solution of zincic oxide, and adding to it a small quantity of alcohol, long needles were obtained, which he considered a "bi-zincate of potassa." It was immediately decomposed by water into zincic oxide and potassic hydrate. A few years later, in his article in the *Annales de Chimie et de Physique*,[2] Fremy states that he has met with great difficulties in obtaining the crystals, and hopes to return to the subject when he has determined the conditions under which they are formed. Neither of his papers contains analyses, and he has never published anything more on the subject, the reason for which we can well understand after our unsuccessful attempts to prepare potassic zincates.

The work on the ammonic zincates has led to about the same unsatisfactory results, no analyses of laboratory products having been published; but Malaguti[3] gives an analysis of an incrustation found upon a brick in the vault of a privy, which had the composition $3ZnO.4NH_3.12H_2O$.

The only other research which has approached this subject is one by Prescott,[4] published in 1880, on the solubility of zincic oxide in caustic alkalies. He found that more alkali is needed for complete solution of the zincic oxide than would be required by the following reaction,

$$ZnSO_4 + 4KOH = Zn(OK)_2 + K_2SO_4 + 2H_2O,$$

but this excess was smaller in the case of sodic or ammonic hydrate than with potassic hydrate; also that the excess of alkali could be neutralised in such a solution without precipitating zincic hydrate, until the amount was reached indicated by the reaction given above. Addition of a large quantity of water precipitated the zincic hydrate from the solution, even when it contained the excess of alkali. The effect of dilution and temperature on the solubility was also studied, but the determination of the composition of the substances formed did not come within the scheme of his work.

[1] Comptes Rendus **15**, 1106.
[2] Ann. chim. phys., Ser. **12**.
[3] Comptes Rendus **62**, 413.
[4] Chem. News **42**, 30.

As, therefore, we could find in the chemical literature no analyses of a zincate, with the exception of Malaguti's ammonic zincate, we decided to take up the subject, and fortunately began our work with the sodic zincate, since this proved to be the one of them all which can be most easily prepared.

The principal results which we have obtained can be briefly summarised as follows: From a solution of zincic oxide in aqueous sodic hydrate, two crystalline sodic zincates can be separated by the action of alcohol; the principal product, which fuses below 100°, has the formula $Zn_3O_6Na_4H_2.17H_2O$; the other, which does not fuse at 300°, is $(ZnO_2NaH)_2.7H_2O$. Both substances are decomposed into zincic oxide and sodic hydrate by water or alcohol. We had hoped at first to extend our work to other zincates, but, after a number of experiments, have abandoned this intention, as with potassic hydrate no crystalline or definite compound could be obtained, and although ammonic hydrate gave a product crystallising in needles, it was obtained with difficulty, and proved to be of varying composition. We give, however, at the end of this paper, a brief account of the negative results of these experiments, and of some others in similar directions.

Preparation of the Sodic Zincates.

The sodic zincates can be prepared by the action of sodic hydrate on either metallic zinc, zincic oxide, or zincic hydrate, and the product seemed to be the same in every case. It is most convenient, therefore, to prepare them from zincic oxide, as the metallic zinc dissolves very slowly, long boiling with aqueous sodic hydrate being necessary to prepare a sufficiently strong solution. On the other hand, we have not succeeded in preparing the sodic zincates from sodic carbonate, as a mixture of this substance with zincic oxide showed no loss of weight even when kept at a white heat for some time. The method adopted by us consisted in dissolving zincic oxide in a strong aqueous solution of sodic hydrate,[1] with the aid of heat, in a flask, which was usually closed with a cork fitted with a set of potash bulbs, to prevent the absorption of carbonic dioxide by the alkaline liquid, but this precaution was not absolutely necessary. The solution, after it had cooled, was treated with twice or three times its volume of alcohol, and the mixture, after being thoroughly shaken, allowed to stand

[1] The sodic hydrate used by us had been purified by alcohol.

securely corked for about twenty-four hours. During this standing two layers were formed, a heavy aqueous solution and a lighter alcoholic liquid. These were separated, the aqueous solution treated again with alcohol in the same way, and this extraction with alcohol repeated until the heavier portion solidified shortly after it had been removed from the alcohol, which happened usually after the third or fourth extraction. The crystalline mass thus obtained we have called fusible sodic zincate, because it melts below 100°. The second sodic zincate was obtained from the alcoholic washings, which were mixed, and allowed to stand in a corked flask, when after some time, which varied from a few hours to several days, white crystals were deposited on the sides of the flask, which gradually increased in quantity. The formation of these crystals did not occur invariably, but they could often be made to appear by adding more alcohol to the washings. This compound deposited from the alcoholic washings does not fuse even at 300°, and we shall call it infusible sodic zincate.

Analysis of the Fusible Sodic Zincate, $Zn_3O_6Na_4H_{32}.17H_2O$.

This substance is the principal product of the reaction, forming, as nearly as we could estimate, over 90 per cent. of the total product. Since both water and alcohol decompose it, a further purification seemed impossible, and we were obliged to analyse it as it was obtained by the precipitation with alcohol, simply drying it by pressure between filter paper under heavy weights.

The method of analysis, which we adopted after trying several others, consisted in dissolving the substance in dilute sulphuric acid, and precipitating the zinc by means of a measured quantity of a standard solution of sodic carbonate. The zinc was weighed as oxide. The filtrate was acidified with sulphuric acid, evaporated to dryness, weighed, and then the amount of sodium calculated after subtracting from the total weight of the sodic sulphate the weight of sodic sulphate corresponding to the sodic carbonate added.

I. 0.4720 gram of the substance gave 0.1744 gram of zincic oxide and 0.2080 gram of sodic sulphate.

II. 0.6420 gram of the substance gave 0.2302 gram of zincic oxide and 0.2718 gram of sodic sulphate. 0.8802 gram of substance from the same preparation lost at 240° 0.3920 gram of water,

and the dried product gave, on heating with chromic oxide in a stream of dry oxygen, 0.0342 gram of water.

III. 0.9682 gram of the substance gave 0.3370 gram of zincic oxide and 0.3992 gram of sodic sulphate. 0.8770 gram of substance from the same preparation lost at 240° 0.4021 gram of water.

	I.	II.	III.
Zinc,	29.66	28.78	27.93
Sodium,	14.28	13.72	13.36
Water,	...	44.54	45.83
Constitutional Water,	...	3.88	...

Each of these three analyses was made with a sample from an entirely separate preparation, in order to determine whether the substance had a definite composition, and when it is remembered that it could not be purified by crystallisation, and was dried only imperfectly by pressing with filter paper, the agreement is as close as could be expected; but it is obvious that in a case like this the atomic ratios are of much more importance than the percentages, and we have accordingly calculated them as follows:

Atomic Ratio of Zinc to Sodium in Fusible Sodic Zincate.

	Zinc	:	Sodium.
I.	1.	:	1.36
II.	1.	:	1.35
III.	1.	:	1.35

The agreement between these numbers proves conclusively that the substance is a definite compound, and that the proportion of zinc to sodium is as three to four. In trying to calculate a formula for it, we have felt much doubt in regard to the amount of water of crystallisation, for the reasons given above; but the one finally adopted by us gives percentages which agree so well with those found that it cannot be far from the truth, especially as the amounts of water found are about as much higher than those calculated as was to be expected. The constitutional water, on the other hand, comes very high, but we do not have much faith in this determination.

	Calculated for $Zn_3O_8Na_4H_2.17H_2O$.	Found I.	Found II.	Found III.
Zinc,	28.28	29.66	28.78	27.93
Sodium,	13.30	14.28	13.72	13.36
Water,	44.24	...	44.54	45.83
Constitutional Water,	2.60	...	3.88	...

To prove that the substance contained water, and not alcohol of crystallisation, a combustion of it was made in the usual manner, but only a mere trace of carbonic dioxide was obtained.

The formula of this substance, $Zn_3O_6Na_4H_2.17H_2O$, agrees, except in water of crystallisation, with that of the substance analysed by Malaguti (see page 146), which, written in the same way, becomes $Zn_3O_6(NH_4)_4H_2.9H_2O$. This, as has been mentioned already, is the only zincate of which an analysis has been published.

We have made only one analysis of another preparation of this substance which is comparable to those given above; this gave about the same percentage of zinc, 29.45, but a much larger amount of sodium, 19.56, which was undoubtedly due to a small quantity of sodic hydrate left adhering to the crystals, as this was the first preparation we made, and therefore was not pressed out so thoroughly as the later ones, after we had become more familiar with the manipulation.

Properties of the Fusible Sodic Zincate.

The substance as precipitated by alcohol from its solution in aqueous sodic hydrate forms a white mass, made of radiating crystals, often of considerable size. It fuses at about 70°, but, owing to the difficulty of drying it, no attempts were made to determine the melting point accurately. Water decomposes it rapidly and completely, converting it into a white insoluble powder, which gave on analysis the following result:

0.1990 gram of the substance gave 0.1910 gram of zinc oxide and no sodic sulphate.

	Calculated for ZnO_3H_2.	Calculated for ZnO.	Found.
Zinc,	65.72	80.28	77.03

The substance therefore seems to be principally zincic oxide mixed with a slight impurity of the hydrate. Alcohol decomposes it in a similar way, but more slowly, as is shown by the following percentages obtained from the analyses of two preparations (IV, V), which we had attempted to purify by washing with alcohol:

	III.	IV.	V.
Zinc,	27.93	29.96	33.36
Sodium,	13.36	12.27	10.48

III is one of the analyses already given. The substance for this analysis was only pressed with filter paper. IV was a sample

which had been washed three times with common alcohol, while the substance which had the composition given under V had been washed four times with absolute alcohol. These numbers show that the action of the alcohol consists in gradually removing the sodium as sodic hydrate, and this point is brought out even more sharply by a comparison of the atomic ratios.

	Zinc	:	Sodium.
III.	1.	:	1.35
IV.	1.	:	1.16
V.	1.	:	0.89

It follows from what has been said on this subject that care must be taken not to continue longer than is absolutely necessary the treatment with alcohol during the preparation of the sodic zincate. Although the substance is decomposed by both alcohol and water, it seems to exist during the process of manufacture dissolved in a mixture of these solvents in presence of an excess of sodic hydrate, an observation which is confirmed by that of Prescott (see page 146). It is insoluble in ether, and absorbs carbonic dioxide rapidly from the air. At 100° it loses only 12 molecules of its water of crystallisation, as is shown by the following analysis:

0.4720 gram of the substance analysed under I, when heated to 100° in a stream of pure dry air, lost 0.1510 gram of water.

	Calculated for a loss of $12H_2O$.	Found.
Water,	31.23	32.00

Analyses and Properties of the Infusible Sodic Zincate, $(ZnO_2NaH)_2.7H_2O$.

This substance, which crystallises from the alcoholic washings obtained in the preparation of the fusible compound just described, is formed in comparatively small quantities. As nearly as we could estimate, only a few per cent. of the total product consisted of it. As, like the fusible compound, it is decomposed by both water and alcohol, no attempt was made to purify it further, but it was analysed after drying at ordinary temperatures by the method already described (see page 148).

I. 0.7470 gram of the substance gave 0.3424 gram of zincic oxide and 0.2913 gram of sodic sulphate; 0.4762 gram of substance from the same preparation lost at 220° 0.1637 gram of water.

II. 0.6044 gram of the substance lost at 300° 0.2066 gram of

water, and gave 0.2700 gram of zincic oxide and 0.2355 gram of sodic sulphate.

	Calculated for $(ZnO_2NaH)_2.7H_2O$.	Found. I.	Found. II.
Zinc,	35.32	36.78	35.86
Sodium,	12.50	12.62	12.62
Water,	34.24	34.37	34.19

The considerable difference between the percentages of zinc is not greater than was to be expected, when the impossibility of purifying the substance is remembered. Each of these analyses was made with a sample from a separate preparation, and we add the following analysis, made early in the work simply to determine the ratio between the zinc and sodium, no care having been taken to dry the substance.

III. 0.7025 gram of slightly moist substance gave 0.2260 gram of zincic oxide and 0.1951 gram of sodic sulphate.

The percentages derived from this analysis are of course of no value, but it gives an atomic ratio which agrees with those from the preceding analyses so closely that there can be no doubt that this substance possesses a definite composition.

Atomic Ratio of Zinc to Sodium in the Infusible Sodic Zincate.

	Zinc	:	Sodium.
I.	1.03	:	1.
II.	1.03	:	1.
III.	1.02	:	1.

A combustion of the substance showed that it contained no alcohol.

This substance undoubtedly corresponds to the crystalline body obtained by Fremy (see page 146), who assigned to it the same ratio between the zinc and potassium. Laux (see page 145), on the other hand, ascribed to his crystals, which were soluble in water, the formula ZnO_2K_2, but stated that upon heating these crystals he obtained an amorphous powder which showed the ratio of 1 : 1 between zinc and potassium; that is, the same obtained in the crystals by Fremy and us. We have met with no substance corresponding to the soluble crystals of Laux.

Properties.—The infusible sodic zincate crystallises from a solution in dilute alcohol containing an excess of sodic hydrate in white needles, sometimes over a centimeter long, forming loose

radiating groups usually of a conical shape, but occasionally circular or spherical. It does not melt even at 300°, and is decomposed by alcohol, or water, if these solvents are free from sodic hydrate, absorbs carbonic dioxide from the air, but much less rapidly than the fusible compound, and does not lose the whole of its water of crystallisation until heated above 200°.

We have not succeeded in finding any other definite compound among the products of the action of sodic hydrate on zincic oxide, and if any other exists, it can be only in very small quantity.

After we had settled the composition of the sodic zincates, we turned our attention to the study of other zincates, and also tried some experiments with magnesic oxide. The results of all this work were negative, but nevertheless we think it best to give a brief statement of what we have done.

In all our attempts to prepare potassic zincate we encountered the difficulties already mentioned by Fremy; in fact, we have not succeeded in obtaining in any experiment the crystals described by him, although we have modified the process employed in a number of different ways; but the solution of zincic oxide in potassic hydrate, when treated with alcohol according to the method which had yielded such good results with sodic zincate, gave only amorphous precipitates, which looked like zincic oxide, but were not wholly free from potassium; as the absence of crystalline form left us no means by which we could judge of the purity of this substance, we did not think it worth analysis.

With ammonic hydrate the results looked more promising at first, as the solution of zincic hydrate in ammonic hydrate occasionally gave a small quantity of crystals, after it had been mixed with alcohol and allowed to stand; but in this case there was no separation of the liquid into two layers. These crystals looked very much like the infusible sodic zincate described above, but the analyses of four preparations showed that they had no constant composition, the following percentages being obtained:

	I.	II.	III.	IV.
Zinc,	48.66	45.90	...	59.96
Ammonia,	7.35	4.58	3.67	5.28

In view of these results it did not seem worth while to continue the investigation.

In beginning this research we had hoped, by acting on the sodic zincate with a cobaltous salt, to obtain Rinman's green, and in this

way throw some light on the composition of this pigment. These hopes have not been fulfilled, as the zincates were decomposed by alcohol or water, as already stated, and therefore the action could not be carried on in solution, and the melted fusible zincate, when treated with cobaltous chloride, gave only a blackish precipitate with no shade of green. The same result was obtained when an ethereal or absolute alcohol solution of cobaltous chloride was allowed to act on the zincate. We have also made many attempts to purify Rinman's green, prepared according to the usual method, in order to fit it for analysis, but none of these have succeeded, the substance being decomposed by solutions of alkalies or acids, in fact even by a solution of carbonic dioxide under pressure, which dissolved both zincic and cobaltous carbonates, and finally left a blackish gray residue.

Although magnesic hydrate does not dissolve in sodic hydrate under ordinary conditions, we thought that possibly a very strong solution of sodic hydrate might have some solvent action at its boiling point, and upon trying the experiment, obtained long prismatic crystals, which, however, we found contained only a mere trace of magnesium (0.39 per cent.), and consisted of the crystallised sodic hydrate recently obtained by Cripps,[1] as shown by the following analytical results:

I. 0.5620 gram of the substance lost 0.2150 gram of water.

II. 0.4115 gram of the substance gave 0.4585 gram of sodic sulphate.

	Calculated for $(NaOH)_2.4H_2O$.	Found. I.	Found. II.
Water,	37.50	38.26	...
Sodium,	35.93	...	36.11

The curious point about this observation, which alone makes it worth recording, is that the solution of sodic hydrate used could not be made to crystallise before it was treated with magnesic oxide, but after such treatment crystallised so rapidly that it was impossible to filter it. The experiment was repeated several times, each time with the same result. What the cause of this difference in behavior may be we have been unable to determine, but think that possibly a small quantity of sodic carbonate in our solution of sodic hydrate may have prevented the crystallisation, which took place as soon as this was converted into hydrate by the magnesic oxide.

[1] Pharm. Jour. Trans., Ser. 3, **14**, 833 (1884).

ON THE ATOMIC WEIGHT OF OXYGEN.

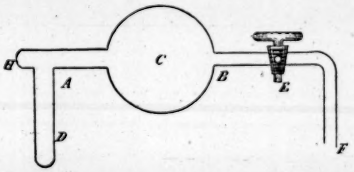
By W. A. Noyes.

The great importance which attaches to the atomic weight of oxygen makes it very desirable that this constant should be determined by several methods and by independent workers.

The method to be described was suggested to the author of this paper when reading Keiser's first paper.[1] A somewhat similar method has been proposed for a different purpose by Morley.[2]

The results which I have thus far obtained I consider as only preliminary, and they are presented now because it is necessary to discontinue the work for some time, and because they may be of some interest to others who are working in the same field.

The fundamental idea of the method is that by passing hydrogen into an apparatus containing hot copper oxide, and condensing the water formed within the same apparatus, the weight of the hydrogen can be determined by the gain in weight of the apparatus. The form of apparatus which was found best suited for the purpose is illustrated in the accompanying cut. It was made by Emil Greiner in New York.



C is a bulb with a capacity of 30 to 50 cc. and will contain 90 to 150 grams of copper oxide. The tube *H* was open when the apparatus was received from the maker. A small plug of asbestos was first placed at *B*, the bulb *C* was filled with carefully ignited copper oxide (Kahlbaum's best in wire form), and the tube was sealed at *H*. The volume of the apparatus was then determined by weighing in air and in water, and a counterpoise of nearly the same volume and of somewhat less weight was prepared. The

[1] Ber. d. chem. Ges. **20**, 2323.

[2] This Journal **10**, 22.

tube F was then connected with a Sprengel pump by means of a bulb containing phosphorus pentoxide, and the air was pumped out. During the exhaustion the bulb was heated in an appropriate air-bath. After exhaustion, the apparatus was allowed to cool and was then weighed, using the counterpoise before mentioned. The balance used was made by Ruprecht in Vienna, and the weight of the apparatus (150 to 220 grams) could easily be determined to $\frac{1}{10}$ milligram. The apparatus was always allowed to stand in the closed balance-case for several hours, and usually over night, before the weight was finally determined. The volume of the counterpoise and weights was the same as that of the apparatus, within 1.5 cc. in every case, and usually somewhat closer. The greatest difference of temperature between the two weighings which gave the hydrogen was four degrees, and the greatest difference in pressure was seven millimeters. Supposing the differences to have occurred at the same time and in the same direction, and the difference in volume to have been 1.5 cc., the error from this source would have been four one-hundredths of a milligram.

No correction to vacuum was necessary, as all of the weights for a determination were made with an apparatus of the same volume, and were determined with weights whose relative values had been determined by calibration *in the air*.

After weighing, the apparatus was again placed in the air-bath and heated while it was connected with an apparatus giving carefully purified hydrogen. The connection at F was sometimes made with a short piece of rubber tubing, the two tubes being brought together within it and the whole covered with mercury to prevent possible leakage or diffusion, and sometimes by a ground glass joint lubricated with a little grease. Each method seemed to serve equally well, except in one case, when a little mercury was drawn in through the rubber joint. In that case a low result was obtained, probably because of the vapor of mercury taken up by the hydrogen. When the hydrogen is first admitted to the apparatus through the three-way cock, it rushes over the copper oxide, and only a part of it is converted into water. Very soon a condition is reached when the side-tube D is filled with hydrogen, while the bulb is filled with nearly pure water-vapor. The hydrogen slowly diffuses back to the copper oxide, where it is converted into water-vapor, while the water-vapor diffuses into D and is condensed. The tube A and the opening into D are made about one cm. in

diameter, that the diffusion may be as rapid as possible. *D* is cooled by immersion into distilled water. From two to four liters of hydrogen can be passed into the apparatus and converted into water in an hour. In a part of the experiments, the results of which are given below, a U-tube was used in place of the bulb to contain the copper oxide, but that form of apparatus was found less suitable.

After passing in a suitable amount of hydrogen, the stop-cock was closed, and by continuing the heating for a short time, all of the *gaseous* hydrogen was converted into water. The apparatus was then cooled and weighed with the same precautions as at first. The apparatus was then connected with a Sprengel pump by means of a bulb surrounded with ice-water. After exhausting the bulb and the tube *F*, the stop-cock was turned, and the small amount of nitrogen which always remained in the apparatus was pumped out and delivered into a eudiometer, where it was measured and further examined. Meanwhile the tube was heated in the air-bath, and the tube *D* was surrounded with hot water. As the water in *D* had been for several hours in an almost perfect vacuum, the water on the outside could be heated to boiling without fear of any ebullition within the tube. The water evaporated quite rapidly from the surface, and 6 or 8 cc. could be expelled from the apparatus in about an hour. In some of the experiments the apparatus was then connected with a vacuous bulb filled with phosphorus pentoxide, while in others it was cooled and weighed without this step. The vapor remaining in the apparatus in the latter case was very small in amount, and was determined along with the water obtained by reoxidising the reduced copper. After cooling and weighing, the apparatus was again placed in the air-bath and heated, and oxygen from a gasometer was passed in. The oxygen was passed over heated copper oxide, through a strong solution of caustic potash, and over stick potash and phosphorus pentoxide.

At this point arose one of the most serious questions with regard to the process. It was found that, even after very prolonged heating in pure oxygen, the copper would not take up as much oxygen as had been taken from it by the hydrogen. The explanation seems to be that the hydrogen, as it reduces the copper oxide, leaves the copper in a porous condition, so that the last traces of oxygen can be taken from it by the hydrogen. When the oxygen

is passed in, however, the copper on the surface is oxidised first and the copper oxide formed, filling a greater volume than the copper; the pores are almost or quite closed, and the copper within is protected from further oxidation. Whether the copper loses all of the hydrogen which it has absorbed, as Keiser has shown that palladium does, is, perhaps, a question. The only direct evidence which has been thus far obtained on this point was one case in which the copper was heated twice in an atmosphere of oxygen. On the first heating it absorbed two grams of oxygen and gave 0.0160 gram water. On thes econd heating the copper absorbed one-half gram of oxygen and gave only 0.0013 gram water. The heating in the second case was continued for two hours. In other cases the heating was continued much longer, and the reoxidation was still far from complete. Even in some cases when copper reduced in hydrogen and reoxidised in oxygen was used, the copper could not, after a second reduction, be made to take up the same amount of oxygen again. If the copper remaining unoxidised still retained hydrogen, it would seem that the determinations of Cooke and of Keiser must have been subject to an error from the same source. Such an error must have been very small, but it is desirable that some determinations should be made by means of another agent than copper oxide.

After passing in the oxygen, the apparatus was cooled and weighed. It was then heated again, and the gases remaining in it pumped out into a eudiometer, while the water formed was received in a bulb filled with phosphorus pentoxide. On cooling and weighing, the loss of weight, less the weight of the gases pumped out, as determined by analysis, gave the weight of water obtained from the hydrogen which had been absorbed by the copper. Errors in any of these last weights would have only one-ninth as great an effect on the result as errors in the weights by which the amount of the hydrogen was determined. The amount of the water obtained after the oxidation of the copper was quite variable, partly because in some cases the bulb was only connected with the vacuous bulb surrounded with ice-water before reoxidation and so remained filled with aqueous vapor at a very low tension, and partly because the copper oxide used had been reduced and only partly reoxidised as stated above, and in such cases the amount of metallic copper was much greater in proportion to the amount of water fisrt formed than in other cases.

The hydrogen was prepared from pure (?) zinc and pure hydrochloric acid. The latter was of specific gravity 1.12, and was boiled carefully and partly cooled in a current of hydrogen before it was introduced into the flask from which it was fed to the generator. Also, pieces of pure zinc were put into it, to more thoroughly wash out dissolved gases and to furnish nascent hydrogen which should remove the last traces of oxygen from the liquid. Contact with the air was carefully avoided, and the acid was fed into the generator from a flask filled above with hydrogen, either by an arrangement similar to that described by Cooke, or with hydrogen from an independent generator. After the introduction of the hydrochloric acid into the feed-flask, a solution of blue chromous chloride was added. This was obtained by the reduction of potassium pyrochromate with zinc and hydrochloric acid. Its purpose was to absorb any traces of oxygen, and to give evidence of any air in the apparatus, by its change in color. The heavy flask used for a generator had a capacity of one liter, and had but one neck. The rubber stopper, bearing four tubes, was sunk into the neck, and covered with a thin layer of mercury, to prevent possible diffusion. The acid was fed by a siphon, and only its vapor came in contact with the stoppers. When hydrogen from the generator was used in the feed-flask, the stopper of the latter was surrounded with a jacket filled with mercury.

From the generator the hydrogen was passed through a 20-bulb tube filled with a 30 per cent. solution of caustic potash, to which some lead chloride was added. The latter revealed the presence of a small amount of hydrogen sulphide. Next was an 8-bulb tube containing a 3 per cent. solution of potassium permanganate, then a layer of hot copper. This was omitted in the first determinations, and was introduced from fear of a trace of oxygen from the potassium permanganate. After its introduction, a trace of hydrogen sulphide was found in the strong caustic potash solution which followed. This may have come from the rubber joints at both ends of the tube containing the copper. These joints could not be sealed, as they were between hard and soft glass. The joint at the other end of the potassium permanganate tube was also of rubber, because the solution required frequent renewal. The tubes were brought close together within these joints, and they were covered with jackets filled with water, to prevent diffusion. All other joints were made by fusing the

glass together. After the copper, the hydrogen passed a strong caustic potash solution, to which lead sulphate was added in the later experiments, and then over stick potash and over phosphorus pentoxide mixed with asbestos. Glass-wool was avoided, because a specimen examined was found to have so low a specific gravity as to prove that it consisted—in part, at least—of fine glass tubes, and it was feared that the air in these would diffuse out slowly and mix with the hydrogen. After passing the phosphorus pentoxide an overflow tube was provided, dipping under mercury.

In calculating the results, the weight of the hydrogen, determined by the gain in weight of the apparatus, was corrected by subtracting the weight of the gas which was obtained in removing the water formed, as described above. This gas was calculated as nitrogen. In every case but one, however, oxygen was added in excess, then hydrogen, and the mixture was exploded. The results would seem to indicate that the gas contained from six to eleven thousandths of a milligram of hydrogen, but it is believed that this apparent result came from the formation of a small amount of oxides of nitrogen by the explosion. The oxygen was determined by the loss in weight of the apparatus after the water was removed. To this was added eight-ninths of the weight of the water obtained by reoxidising the copper.

Two determinations are omitted in the results given below. In one of these, mercury leaked by the rubber joint, and some of its vapor probably entered with the hydrogen. In the other, a small amount only of the hydrogen was used, and the accidental error was probably large. The other determinations were as follows:

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by reoxidation.	Corrected hydrogen.	Corrected oxygen.	Per cent. of oxygen reabsorbed.	Atomic weight.
1.	0.9449	7.4785	0.0006	0.0215	0.9443	7.4976	31	15.880
2.	0.6760	5.3521	0.0016	0.0034	0.6744	5.3551	28	15.881
3.	0.7879	6.2432	0.0013	0.0137	0.7866	6.2554	43	15.905
4.	0.5527	4.3483	0.0006	0.0420	0.5521	4.3856	61	15.887
5.	0.4278	3.3366	0.0004	0.0631	0.4274	3.3927	65	15.876
6.	0.8271	6.5437	0.0006	0.0249	0.8265	6.5658	27	15.888

Mean = 15.886 ± .0028

It is of special interest to compare this result with that obtained by Cooke, who prepared his hydrogen from the same materials. His result was 15.869, and the probable error of his first series is one half greater than that of this series, while that of his second

series is but little less than this. *If the correction for nitrogen is omitted, the mean of these determinations becomes* 15.867, *or almost exactly the same as Cooke's final mean.* It seems to the author that the evidence is almost conclusive that Cooke's hydrogen was contaminated with a trace of nitrogen. While the amount of nitrogen can be rendered very small (in one case less than ½ cc. in ten and one-half liters), it would seem to be impossible to entirely exclude it with such generators as Cooke and myself have used.

In this series, the apparatus for purifying the hydrogen and also the condition of the copper oxide were repeatedly varied, in the endeavor to discover sources of constant error. One determination has also been made, using dilute sulphuric acid instead of hydrochloric. The result was 15.874.

The results obtained show that the accidental errors of the determination have been made very small. When the result is compared with that obtained by Keiser, however, I am inclined to believe that there must be in these determinations, as well as in those of Cooke, some source of constant error which has not yet been discovered.

Rose Polytechnic Institute, *Dec.* 15, 1888.

ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.

VI.

By W. A. Noyes and W. B. Wiley.

Oxidation of Para-nitro-ortho-toluene-sulphamide.

In previous papers[1] it has been shown that when ortho-sulphamides are oxidised with potassium ferricyanide, ortho-sulphaminebenzoic acids are obtained. Fahlberg[2] has shown that some of these acids may also be obtained by oxidation with potassium manganate and by boiling sulphinides with a solution of caustic potash, or by evaporating to dryness with the latter.

The first oxidations of the nitro-toluene sulphamide were made

[1] This Journal **8**, 176, and **9**, 93.

[2] Ber. d. chem. Ges. **21**, 243.

with potassium ferricyanide, as described in previous papers, and the ortho-sulphamine acid was obtained as expected. Some oxidations were also made with potassium manganate prepared by the directions of Fahlberg,[1] and also with an alkaline solution of potassium manganate, prepared by partially reducing a strongly alkaline solution of potassium permanganate with alcohol. An attempt was also made to obtain the acid by boiling the potassium salt of the corresponding sulphinide with a three per cent. solution of caustic potash. The sulphamine acid seems to be formed in this way, but its formation is accompanied by a deeper-seated decomposition, and the products obtained were difficult to separate. The most satisfactory method of those tried was to boil the sulphamide with a strongly alkaline solution of potassium permanganate. 30 grams of caustic potash and 8 grams of potassium permanganate were dissolved in about 150 cc. of water, and the solution was heated to boiling by passing steam into it. 5 grams of the amide were then added and the solution shaken vigorously. The oxidation took place rapidly and the permanganate was reduced in a few minutes. A three per cent. solution of potassium permanganate was then added in small portions and the solution was heated with steam. As soon as the solution remained green for several minutes after the addition of a new portion of the permanganate, the last portions of the manganate were reduced with alcohol, the solution was filtered, the filtrate was very nearly neutralised with hydrochloric acid and was evaporated to a small bulk. The solution was then made strongly acid and was extracted with ether. The acid remaining after distilling the ether was converted into the barium salt, the solution of the latter was evaporated to dryness and treated repeatedly with alcohol to remove a small amount of the unoxidised amide. The salt was then crystallised from water, and from the crystallised salt the acid was separated by means of hydrochloric acid. After filtering off, it was recrystallised from water.

Para-nitro-ortho-sulphamine-benzoic Acid.

The acid separates, on cooling its hot solution, in small granular crystals which are almost white. These melt at 172° if heated quickly. If heated more slowly they melt at 177°, but if kept for a short time at that temperature they are converted into the

[1] Loc. cit.

sulphinide, and, after solidifying, melt at 209°. The acid is easily soluble in alcohol, quite easily soluble in ether, and rather difficultly soluble in water.

I. 0.1052 gram of the acid gave 0.1002 gram $BaSO_4$.

II. 0.1015 gram of the acid gave 0.0959 gram $BaSO_4$.

	Calculated for $C_6H_3\begin{cases}CO_2H\\SO_2NH_2\\NO_2\end{cases}$.	Found. I.	II.
S	13.01	13.09	12.99

Barium Nitro-sulphamine-benzoate, $\left(C_6H_3\begin{cases}CO_2\\SO_2NH_2\\NO_2\end{cases}\right)_2 Ba + H_2O$.—This was obtained and purified as described above. The salt may also be crystallised from alcohol. It separates from the solution in hot alcohol, on cooling, in fine feathery needles. These contain one molecule of water. The salt crystallised from water contains a larger amount of water, but loses a part of it easily on air-drying, and when dried over sulphuric acid appears to contain but one molecule of water. The analyses, however, are not very accordant. The salt loses its water at 105°, but after being dehydrated at that temperature, the same amount of water is quickly regained on exposure to the air. When heated to 135° the salt loses weight slowly, and is, apparently, converted into the salt of the corresponding sulphinide. At a higher temperature the loss in weight indicates that the conversion is quantitative. The salt of the sulphinide loses its water easily at 105°. Analysis II, below, was with a salt crystallised from alcohol. The other analyses were with salts crystallised from water. All but the first were dried over sulphuric acid.

I. 0.2021 gram of the salt gave 0.0719 gram $BaSO_4$.

II. 0.2066 gram of the salt lost 0.0049 gram H_2O at 105° and gave 0.0736 gram $BaSO_4$.

III. 0.1403 gram of the salt lost 0.0037 gram H_2O at 105° and gave 0.0496 gram $BaSO_4$.

IV. 0.3230 gram of the salt lost 0.0121 gram H_2O at 105° and gave 0.1161 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}CO_2\\SO_2NH_2\\NO_2\end{cases}\right)_2 Ba + H_2O$.	Found. I.	II.	III.	IV.
H_2O	2.79	...	2.37	2.64	3.83
Ba	21.24	20.90	20.93	20.77	21.12

Silver Nitro-sulphamine-benzoate, $C_6H_3\begin{cases}CO_2Ag\\SO_2NH_2\\NO_2\end{cases} + \frac{1}{2}H_2O$. —

This was prepared by adding silver nitrate to the hot solution of the barium salt. On cooling, the salt separated in short, thick needles of a light yellow color. The salt loses nothing over sulphuric acid, and loses water but slowly at 105°.

I. 0.1070 gram of the salt gave 0.0317 gram Ag.

II. 0.1167 gram of the salt lost 0.0020 gram H_2O at 135° and gave 0.0348 gram Ag.

III. 0.1221 gram of the salt lost 0.0028 gram H_2O at 135° and gave 0.0365 gram Ag.

	Calculated for $\left(C_6H_3\begin{cases}CO_2\\SO_2NH_2\\NO_2\end{cases}\right)_2 + \frac{1}{2}H_2O$.	Found. I.	II.	III.
$\frac{1}{2}H_2O$	2.49	...	1.71	2.29
Ag	29.83	29.63	29.82	29.89

Di-silver Nitro-sulphamine-benzoate, $C_6H_3\begin{cases}CO_2Ag\\SO_2NHAg\\NO_2\end{cases} + H_2O$.

—This salt was prepared by adding a very small amount of ammonia to the mother-liquors of the last salt. It separated at first as an amorphous precipitate which passed into solution on heating. After filtering and cooling, the salt separated as a greenish yellow crystalline powder. It loses one-half its water at 105°, the remainder at 135°.

0.0577 gram of the salt lost 0.0022 gram H_2O at 135° and gave 0.0260 gram Ag.

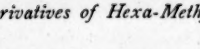
	Calculated for $C_6H_3\begin{cases}CO_2Ag\\SO_2NHAg\\NO_2\end{cases} + H_2O$.	Found.
H_2O	3.76	3.81
Ag	45.19	45.06

Rose Polytechnic Institute, *Dec.* 17, 1888.

SOME DERIVATIVES OF HEXA-METHYLENE.

By Paul C. Freer and W. H. Perkin, Jr.[1]

The substance previously described as methyl-dehydrohexone-carboxylic acid,



when boiled with water, yields aceto-butyl alcohol,

$$CH_3.CO.CH_2.CH_2.CH_2OH.$$

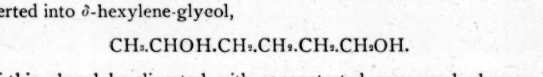
This substance, when treated with sodium amalgam, is easily converted into δ-hexylene-glycol,

$$CH_3.CHOH.CH_2.CH_2.CH_2.CH_2OH.$$

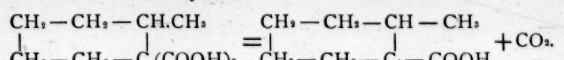
If this glycol be digested with concentrated aqueous hydrogen bromide, the corresponding methyl-penta-methylene dibromide results,

$$CH_3.CHBr.CH_2.CH_2.CH_2.CH_2Br.$$

By the action of the sodium compound of malonic ether on this dibromide, hexa-methylene derivatives can be obtained, according to the following equation:



The resulting substance has been called ethylic methyl-hexa-methylene dicarboxylate (2.1.1.). This ether on saponification yields free methyl-hexa-methylene dicarboxylic acid, which latter, when distilled, decomposes into the corresponding mono-carboxylic acid and carbonic anhydride:



[1]Abstract of a paper which appeared in the Journal of the Chemical Society (London), Vol. 53, p. 202. Communicated by the authors.

Ethylic methyl-hexa-methylene dicarboxylate is a thick, colorless oil, of disagreeable odor, boiling between 260°–265°, at 250 mm. pressure. The yield of this substance is not very satisfactory, owing to the formation of a considerable quantity of a higher boiling substance, the constitution of which will be explained in a future paper. The dicarboxylic acid obtained from this ether by means of saponification with alcoholic potash, is a sandy, crystalline powder, melting at 147°, with partial decomposition into the mono-carboxylic acid and carbonic anhydride. It is readily soluble in ether, alcohol, and hot water, more sparingly soluble in cold water. Methyl-hexa-methylene mono-carboxylic acid is a thick, colorless oil, of a most penetrating and disagreeable odor. It boils at 235°–236°. Its physical properties agree closely with the formula assigned to it.

In carrying out this investigation it was thought that interesting results could be obtained by studying the action of methyl-penta-methylene dibromide on the sodium derivative of aceto-acetic ether; as in this case it was doubtful whether hexa-methylene derivatives, or compounds containing a carbon-oxygen ring, would result. In the case of the action of tri-methylene bromide on sodium aceto-acetate, it will be remembered, a body belonging to the latter class was exclusively produced.

If one molecular proportion of sodium aceto-acetic ether be digested with one of methyl-penta-methylene dibromide, a substance $C_{12}H_{21}O_3Br$ is produced. This may have either of the following formulae:

(1) $\begin{matrix}CH_3-CO\\COOC_2H_5\end{matrix}\!>\!CH.CH.CH_2.CH_2.CH_2.CH_2.CH_2Br.$

(2) $\begin{matrix}CH_3-CO\\COOC_2H_5\end{matrix}\!>\!CH.CH_2.CH_2.CH_2.CH_2.CHBr.CH_3.$

Which of these is correct we cannot state, and, as the constitution of the substance subsequently obtained is not affected thereby, we have not attempted to distinguish between them.

If this bromine compound is treated with zinc-dust and acetic acid, the bromine atom is readily replaced by hydrogen. To determine the constitution of the above compound it would, therefore, only be necessary to compare this reduction-product with hexyl-aceto-acetic ether. If the substance be identical with this latter, formula 2 would be correct; if isomeric, formula 1 must be assigned to it.

The bromine compound $C_{12}H_{21}BrO_3$, when treated with sodic ethylate, or the sodium compound of aceto-acetic ether, is converted into ethylic acetyl-methyl-hexa-methylene carboxylate,

$$\begin{matrix} CH_3-CO \\ COOC_2H_5 \end{matrix}\!\!>\!CH.CH_2.CH_2.CH_2.CH_2.CH_2Br + C_2H_5ONa =$$

$$\begin{matrix} CH_2-CH_2-CH-CH_3 \\ | \qquad\quad | \\ CH_2-CH_2-C<\begin{matrix} COCH_3 \\ COOC_2H_5 \end{matrix} \end{matrix} + NaBr + HOC_2H_5.$$

That the substance so produced is really a hexa-methylene derivative is shown by a study of its decomposition products resulting from saponification. When boiled with alcoholic potash it is easily decomposed, with formation of methyl-hexa-methylene-methyl ketone and methyl-hexa-methylene carboxylic acid, thus:

(1)
$$\begin{matrix} CH_2-CH_2-CH.CH_3 \\ | \qquad\quad | \\ CH_2-CH_2-C<\begin{matrix} COCH_3 \\ COOC_2H_5 \end{matrix} \end{matrix} + 2KOH =$$

$$\begin{matrix} CH_2-CH_2-CH.CH_3 \\ | \qquad\quad | \\ CH_2-CH_2-C<\begin{matrix} COCH_3 \\ H \end{matrix} \end{matrix} + K_2CO_3 + C_2H_5OH.$$

(2)
$$\begin{matrix} CH_2-CH_2-CH-CH_3 \\ | \qquad\quad | \\ CH_2-CH_2-C<\begin{matrix} COCH_3 \\ COOC_2H_5 \end{matrix} \end{matrix} + 2KOH =$$

$$\begin{matrix} CH_2-CH_2-CH.CH_3 \\ | \qquad\quad | \\ CH_2-CH_2-C<\begin{matrix} H \\ COOH \end{matrix} \end{matrix} + K_2CO_3 + C_2H_5OH + CH_3COOK.$$

The methyl-hexa-methylene carboxylic acid obtained in this manner was identical with that obtained by the action of methyl-penta-methylene dibromide on the sodium compound of malonic ether.

If methyl-penta-methylene dibromide be dissolved in ether, and granulated sodium then gradually added, violent reaction sets in; the bromine atoms are entirely eliminated, and a hydrocarbon remains after evaporating the ether. This hydrocarbon gives numbers on analysis which agree with the formula,

$$CH_3-CH\begin{matrix} \diagup CH_2-CH_2 \\ \diagdown CH_2-CH_2, \end{matrix}$$

which is that of a substance which could be called methyl-penta-methylene. The hydrocarbon thus produced boils at 70°–71°,

and seems to be isomeric with all of the hexylenes as yet known. It differs from these in the property of not being attacked by a concentrated aqueous solution of hydrogen iodide. Until a further study shall have fully proved its constitution, however, nothing definite can be said about it.

EXPERIMENTS ON THE SYNTHESIS OF HEPTA-METHYLENE DERIVATIVES.[1]

By Paul C. Freer and W. H. Perkin, Jr.

When malonic ether is treated with methyl-penta-methylene dibromide, two substances are produced. One of these has already been described in the paper on hexa-methylene derivatives; the other, which is formed in considerable quantity, is the product of the reaction of two molecules of malonic ether with one of the dibromide, thus:

$$2(COOC_2H_5)CHNa + CH_3CHBr(CH_2)_3CH_2Br = (COOC_2H_5)_2CH.CH.CH_2.(CH_2)_4CH(COOC_2H_5)_2 + 2NaBr.$$

This ethereal salt, for which we propose the name ethylic isoheptane ($\omega_2\omega_2$) tetracarboxylate, is a colorless oil, boiling at 273°–276° at 60 mm. pressure. This ethereal salt, on saponification, is easily converted into the corresponding acid, and this latter, when heated slowly in a metal bath to 200°, is decomposed into carbonic anhydride and a brownish-colored oil, which was purified by means of conversion into the corresponding ether. This ether is a colorless liquid of peculiar odor, boiling at 307°–308°, under ordinary pressure. The substance so produced is the ethereal salt of methyl-azelaic acid, $COOC_2H_5.CH_2.CH(CH_3).(CH_2)_5COOC_2H_5$. This, when saponified with a solution of caustic potash in methyl alcohol, yields pure methyl-azelaic acid,

$$COOH.CH_2.\overset{\displaystyle CH_3}{\overset{|}{C}}H.CH_2.CH_2.CH_2.CH_2.COOH,$$

a white crystalline substance melting at 43°–44°, separating from solvents as an oil, which only solidifies after standing over sulphuric

[1] Abstract of a paper which appeared in the Journal of the Chemical Society (London), Vol. 53, p. 215. Communicated by the authors.

acid in a vacuum. It is fairly soluble in boiling water, easily so in benzene, ether, and alcohol. Methyl-azelaic acid is isomeric with sebacic acid (m. p. 197°) and heptyl-malonic acid (m. p. 97°–98°).

When the ethereal salt of isoheptane-tetracarboxylate is treated with sodium-ethylate, a disodium compound is produced, owing to the fact that the substance contains two —CH— groups connected each with two carbethoxyles. This disodium compound, when suspended in a large quantity of dry ether, is readily acted on by bromine. This experiment was performed with the hope of effecting the synthesis of hepta-methylene derivatives, thus:

$$(COOC_2H_5)_2CNa-\overset{\displaystyle CH_3}{\overset{|}{C}}H.CH_2.CH_2.CH_2.CH_2.CNa\begin{matrix}\nearrow COOC_2H_5\\ \searrow COOC_2H_5\end{matrix}+Br_2=$$

$$(COOC_2H_5)_2-C\overset{\displaystyle CH_3}{\overset{|}{-}}CH.CH_2.CH_2.CH_2.CH_2-C\begin{matrix}\nearrow COOC_2H_5\\ \searrow COOC_2H_5\end{matrix}+2NaBr.$$

It was found, however, that no hepta-methylene derivative resulted, for on saponification of the oil isolated from the ethereal solution, and subsequent decomposition into carbonic anhydride and an oily acid, this latter proved to be regenerated methyl-azelaic acid. As far as we could see, no other acid was produced. It is difficult to explain what takes place in a reaction of this kind; but one fact is very prominent — no hepta-methylene derivative results. The power of forming closed carbon chains seems to cease when the number of carbon atoms exceeds six.

Contributions from the Laboratory of the New York Agricultural Experiment Station.

IV.—ARTIFICIAL vs. ANIMAL DIGESTION.

By E. F. Ladd.

By means of the artificial digestion of feeding-stuffs, we can determine the relative digestibility for the albuminoids of the several substances, and the coefficients obtained serve as a measure of the digestibility of the fodder. That the coefficients obtained

in artificial digestion correspond with the results obtained in actual digestion with animals is not claimed, but that they come quite close (although higher) to those figures may be shown by actual trials in comparison of artificial and animal digestion.

On four occasions, at the New York Agricultural Experiment Station, I have had an opportunity to test the value of artificial digestion as compared with animal digestion, and the results were in round numbers as follows for the albuminoids of the fodders:

	Pepsin digestion.	Animal digestion.
Corn fodder,[1]	54	49
Soja hispida,[1]	75	70
Orchard grass hay,[2]	62	60
Corn meal,[3]	64	58

We see by the above table that the coefficients obtained by artificial digestion for the albuminoids were invariably higher than the results secured with animals.

The digestibility of the albuminoids of corn meal as found in the trial was much lower than has heretofore been given. In this case the digestibility of the meal was determined with cows in ration of hay and corn meal, the digestibility of the hay having been previously determined separately with the same animals and *assumed* to be the same in the ration as when fed alone. It should be noted that the digestibility of corn meal as given, in most cases at least, has been made with hogs, animals very different in all respects from ruminants. With one exception, when a soft corn was used, I have never yet been able to obtain digestion coefficients for the albuminoids of corn meal as high as those given in the German tables, or as found by Jordon[3] in his trials with hogs, but the results given in the previous table for the pepsin digestion stand in about the same relation to animal digestion as in the trials with other feeds. Whether the digestion coefficients for the albuminoids of corn meal as now used are too high for ruminants, or whether in the trial I have reported[4] the digestibility for the albuminoids of the orchard grass hay was largely modified when compounded in a ration, remains to be determined by future investigations. That the digestibility was modified to some extent is probable, but not

[1] This Journal **8**, 434.

[2] Report of New York Agricultural Experiment Station, 1888; Proceedings of the Society for Promotion of Agricultural Science, 1888.

[3] Report of Maine Agricultural Experiment Station.

[4] Proceedings of the Society for the Promotion of Agricultural Science, 1888.

to the degree necessary to bring the figures for corn meal up to those usually given: and why this single anomaly in pepsin digestion?

Taking the results of American digestion experiments and the average of my own for pepsin digestion on similar foods, we have the following parallels:

	Digestion Coefficients.	
	Pepsin.	Animal.
Timothy hay,	52	44
Clover hay,	57	53 to 56
Oat straw,	18	?
Maize fodder,	54	49 to 52

In the above table the figures given for both timothy and clover are the averages for twenty-one samples.

Stutzer, Jordon, and others have shown that the results obtained in animal digestion are below the actual amounts digested by the animals, due to the presence in the feces of biliary products, mucus matter, etc. The amount of the error depends upon the richness in albuminoids of the food under examination. Stutzer also thought that a portion of the albuminoids of feed-stuffs was indigestible, and this he called nuclein. This can hardly be true of all substances, and careful redigestion of several feeds leads us to think that in many fodders all of the albuminoids are in a digestible form. The following shows a few of our results for redigestion with pepsin:

	Per Cent. Albuminoids Digested.		
	First Trial.	Second Trial.	Third Trial.
Wheat,	79	34	29
Timothy hay,	59	29	34
Wheat bran,	77	23	11

How near to a complete digestion of the albuminoids might have been attained by drying the undigested residue, regrinding, and repeatedly digesting, I cannot say, but in each case a considerable quantity was digested in the third trial.

Stutzer, Jordon, and others have concluded from their investigations that if the animal feces are subjected to artificial digestion and the undigested portion taken as that undigested by the animal, then the difference between the total albuminoids and that which remains undigested by artificial digestion will be the real amount digested by the animal. I know of no proof to show that the pepsin solution does not digest from the feces some of the undigested portion of the food. That it may do this seems possible,

from the facts already cited, and that, by redigesting the feces a second time, another portion of the albuminoids is digested, as shown below:

	Per Cent. Digested.	
	No. 1.	No. 2.
First digestion,	18.13	13.10
Second digestion,	8.36	7.18

If we assume that the amount actually digested by the cow is the apparent amount plus that portion digested from the feces by a pepsin solution, then, instead of the digestion coefficient for the albuminoids of orchard grass hay being 60 per cent., it is nearly 68 per cent., or, if we take the amount redigested a second time, it will be considerably increased over the last figures.

From the data at our command we conclude:

1. That pepsin digestion furnishes us a reliable means of determining the digestibility of the albuminoids of our feeding-stuffs, and that this serves as a good criterion of the digestibility of the fodder itself.

2. That the coefficients of digestibility for albuminoids, as usually calculated from animal digestion, are too low.

3. That the digestibility of the albuminoids of corn meal, as given in the German tables, seems to be too high for ruminants.

4. That in many of our feeding-stuffs, all of the albuminoids seem to be in a digestible form.

5. That the digestion of the feces by a pepsin solution may, and probably does in most cases, give us results above what is actually digested by the animal.

GENEVA, N. Y., *September* 8, 1883.

Communications from the Chemical Laboratory of Rutgers College.

XVIII.—LECTURE-EXPERIMENTS WITH NITRIC ACID.

BY PETER T. AUSTEN.

Nitric acid, when in the state of a gas, makes an admirable subject for lecture-experiments. A number of experiments with the liquid form are given in Heumann[1] and other books on experi-

[1] Anleitung zum Experimentiren, p. 125.

mental chemistry, but the following experiments with the gaseous form I have not been able to find described. A flask can be filled with nitric acid gas by placing in it some strong pure nitric acid and boiling. This operation, however, takes some little time and is not always satisfactory, as the flask at first becomes filled with a mist. The better plan is to pour into a quart flask, having a neck wide enough to admit a deflagration-spoon, some commercial concentrated sulphuric acid in sufficient amount to cover the bottom of the flask about half an inch, and add to it ten to twenty grams of potassium nitrate. The potassium salt is better than the sodium salt, as it is less liable to contain nitrites, which will discolor the gas by the liberation of N_2O_3. The nitrate should be added in the form of crystals of about one-quarter of an inch in size. If added in a powdered condition, the mass cakes, and requires considerable shaking to disintegrate it. The coarser kind behaves admirably, and on heating the mixture the gas is liberated quickly and evenly.

The flask is hung free on a stand and a small naked flame applied. The nitric acid gas is liberated in large amounts and expels the air at once. This operation should be done under a hood, although, by regulating the heat carefully, it is easily possible to fill the flask and yet not drive off enough gas to cause discomfort. If the filling is done under a hood, the flask and stand are placed, when needed, on the lecture-table; heat, sufficient to prevent the condensation of the gas, being kept under the flask. The sulphuric acid solution on the bottom of the flask is practically invisible, and does not in any way interfere with the experiments.

Nitric acid acts in all of these experiments, except the last, as an oxidising agent, viz:

$$2HNO_3 = H_2O + N_2O_4 + O.$$

It will therefore serve as a source of oxygen, and its reduction will be indicated by the formation of the red N_2O_4. The strong color of this gas makes some of the experiments very striking. In fact, several of them are worthy of performance in the regular lecture-course. The temperature of the gas lies between 90°–100°. To get the full effect of the phenomena, the experiments should be performed in a partially darkened room, which, while permitting the details of the experiments to be observed, makes the combustions appear more brilliant.

Candle.—A lighted candle continues to burn, giving a brilliant flame surrounded by a large pale halo. The peroxide, N_2O_4, as in all of these experiments, forms at first in a large halo about the flame and eventually fills the flask. As this phenomenon occurs in every case, it will not be mentioned again. Owing to the heat of the gas, the candle melts rapidly. The dropping wax soon sets up an action with the mixture of sulphuric and nitric acids on the bottom of the flask. The experiment should be stopped before this begins.

Wood.—An ignited splinter of wood (a splinter fastened to an iron wire is best) burns energetically. A spark bursts into flame as in oxygen.

Charcoal burns brilliantly. If bark-charcoal is used, the scintillations in the red gas produce an unusually fine effect.

Steel Watch-spring.—The spring should be not over 1½ mm. wide and should be detempered. By winding sulphur-string about the end, igniting and introducing quickly, the steel soon ignites and continues to burn brilliantly, but with an effect quite different from the combustion in oxygen. In this case it is well to put a layer of sand half an inch deep in the flask, to prevent fracture of the bottom by the falling globules of fused iron.

Phosphorus burns with an intensely bright light as in oxygen. It soon volatilises and fills the flask with flame. Here again the tinging of the light by the red peroxide, N_2O_4, produces a peculiar effect.

Sodium takes fire without preliminary heating, and burns with an intense yellow light. A small piece and a deep spoon should be used, so as to avoid any chance of the melted sodium falling into the sulphuric acid, as such an occurrence is dangerous.

Magnesium when ignited burns with its characteristic white light.

Copper, zinc and *antimony* I have been unable to make burn.

Illuminating Gas.—A flame of gas, issuing from a bent-up glass tip, when inserted, continues to burn with a brilliant white center surrounded by a large red halo. At first the flame becomes musical, degenerates into a series of rapid, slight explosions, and is extinguished. The tone varies with the size of the flame. After a certain amount of peroxide, N_2O_4, is formed, the flame is not extinguished, and the musical tone also soon ceases.

Hydrogen sulphide burns with a bright, yellow flame. The

flask becomes filled with thick vapors—probably a cloud of chamber-crystals arising from the action of the sulphur dioxide and water (which result from the combustion of the hydrogen sulphide) on the nitrogen tetroxide.

Hydrogen burns with an intensely white flame resembling the flame of illuminating gas just described. It does not become musical.

Caoutchouc.—A piece of black rubber tube, introduced in a deflagration-spoon, soon fuses and evolves gas, which ignites and burns with a large flame having a bright core and a pale halo. If the caoutchouc is ignited in the air, it burns with a white, smoky flame. When now introduced, the flame entirely loses its luminosity and becomes as described.

Turpentine boils violently and emits white fumes, which soon ignite with a gentle explosion and burn with a luminous flame.

Carbon disulphide does not ignite spontaneously, but when ignited and introduced, it continues to burn energetically. It soon volatilises and fills the whole flask with flame.

Benzene does not ignite spontaneously, but when ignited and introduced, it burns quietly with a white flame.

Ether evaporates and reduces the nitric acid gas to the tetroxide, N_2O_4. When ignited and introduced, it soon volatilises and fills the flask with luminous flame.

Hydrochloric Acid Gas.—A stream of the gas issuing from a turned-up tip did not react, nor could the gas be ignited by applying a flame at the point of mixture between the gases. Heating the tube through which the hydrochloric acid was delivered also failed to effect a decomposition.

Hydrobromic acid gas could not be made to react, although a slight decomposition occurred.

Hydriodic acid gas could not be made to ignite. On passing it into the nitric acid gas, however, decomposition and liberation of iodine gas took place. It is a difficult matter to regulate the evolution of hydriodic acid, so that my failure may have been caused by the irregularity of the pressure. Hofmann[1] has shown that drops of hot fuming nitric acid falling through an atmosphere of hydriodic acid produce a large red flame and deposition of iodine crystals. I shall make another attempt to ignite the gas, using a different form of apparatus.

[1] Ber. d. chem. Gesell. **3**, 658.

Ammonia.—This experiment requires a little skill, but is not difficult. Ammonia is evolved in a six-ounce flask, by heating a mixture of ammonium chloride, slaked lime and water. The flask is clamped to a stand and heated with a small flame. The stop-cock to this burner must be accessible without leaving the experiment, for by it is controlled the evolution of the ammonia gas. The success of the experiment depends on getting the right-sized jet of ammonia gas. The ammonia gas is led into the nitric acid gas by means of a glass jet, the tip of which turns up. This jet is connected with the evolution-flask by a sufficiently long rubber tube. The orifice of the jet should not be less than one-eighth of an inch in diameter; a small jet rapidly clogs and closes. The jet-tube should be about sixteen inches long, so that the rubber connection may not be attacked by the nitric acid gas issuing from the flask. The tube is grasped with a pair of tongs and lowered into the mouth of the flask. As the gases mix, a dense cloud of ammonium nitrate is produced. As soon as the jet is on a level with the mouth of the flask, it should be ignited by means of a wax gaslighter, and at the same instant the jet is lowered into the center of the flask. If the jet is of the right size and the pressure is neither too great nor too small, the ammonia will ignite easily and, on lowering into the flask, will continue to burn with a fine yellow flame. When once in position and burning evenly, the flame can be considerably enlarged by increasing the heat under the ammonia flask. The evolution must be regular, and to this end the flame under the ammonia flask should be protected against draughts.

The flame is a peculiar one, consisting of a yellow center, then a greenish-yellow envelope, and then a carmine-red envelope. As the color of the peroxide, N_2O_4, gets deeper, the flame becomes unusually handsome. The products of combustion are presumably oxides of nitrogen, perhaps free nitrogen, although I have not yet established this. It is a more striking experiment than the combustion of ammonia in a current of oxygen.

This experiment can be performed in a large oxygen globe. In this case the flask from which the ammonia is evolved must be provided with a trapped stand-tube filled with ammonia-water to give a pressure. In this way, or by using a large jet and carefully manipulating a clamp on the rubber supply-pipe, a large flame may be easily obtained.

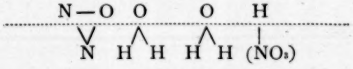
Nitric Oxide.—A jet of nitric oxide, N_2O_2, introduced into nitric acid gas reacts with it, the mixture turning at once red. The product of the reaction is probably nitrous acid,[1]

$$N_2O_2 + 2HNO_3 = 2HNO_2 + N_2O_4.$$

Nitrous Oxide.—A jet of moist nitrous oxide, prepared by heating ammonium nitrate, refuses to ignite in the nitric acid gas. I was surprised to observe, however, the formation of dense white clouds, which on examination proved to be ammonium nitrate. The reaction here is a synthesis of ammonium nitrate:

$$N_2O + 2H_2O + HNO_3 = NH_4NO_3 + HNO_3.$$

The molecule of nitric acid which appears on both sides of the equation is not an instance of chemical tautology, but is demanded, since the rest, NO_2, that appears in the new molecule of NH_4NO_3 is not derived from the $2H_2O$ and the N_2O, but from the HNO_3; for water and nitrous oxide do not unite at a moderate heat. If I interpret the mechanism of this reaction correctly, it should be represented by the following diagram:



ON PARA-NITRO-ORTHO-SULPHOBENZOIC ACID.[2]

By J. H. Kastle.

The investigation, the results of which are recorded in the following pages, was undertaken at the suggestion of Professor Remsen, and carried on under his guidance. The object in view was to throw light upon the chemical conduct of an acid in which the sulphuric acid residue and the carbonic acid residue are in the ortho relation to each other, the point of chief interest being a comparison of the acid with phthalic acid.

[1] Nitric oxide when led through concentrated nitric acid forms nitrous acid. Gmelin-Kraut, 6 ed. I, 2 Aufl. 454.

[2] From the author's dissertation for the degree of Doctor of Philosophy, at the Johns Hopkins University, 1888.

The constitution of phthalyl chloride has for some time been the subject of a good deal of discussion. In 1880 it was pointed out by von Gerichten[1] that the easy formation of phthalid from phthalyl chloride could be most easily explained by assuming that both chlorine atoms are in combination with one and the same carbon atom, and that the anhydride condition exists in phthalyl chloride just as it does in phthalic anhydride itself. At that time the strongest argument against this view was furnished by what was then held to be a fact, viz. that ethers obtained from this chloride by treatment with alcohol and phenol are identical with those obtained from phthalic acid itself. It remained for Graebe[2] to show that these ethers are not identical, as was formerly supposed, but really isomeric—the isomerism being most marked in the case of those obtained from tetrachlorphthalic acid.

In consequence of this, the above argument lost its weight, and since Graebe's investigation on the ethers of phthalic acid, the formula of von Gerichten for phthalyl chloride has been the one most generally accepted, although it must be said that there are still facts on record which speak against this view, particularly that of the formation of phthalimide from phthalyl chloride by the action of gaseous ammonia, a reaction which was found by Kuhara[3] to take place quantitatively, and which can easily be explained on the supposition that phthalyl chloride is made up in this way, $C_6H_4\begin{smallmatrix}COCl\\COCl\end{smallmatrix}$, as was formerly supposed.

In view of all this, the action of phosphorus pentachloride on (*p*)-nitro-sulpho-benzoic acid has been carefully studied, and it has been found that the ethers produced by the action of different alcohols on the chloride thus obtained are not analogous to those obtained by Graebe in the case of phthalyl chloride, but are compounds of this order, $C_6H_3\begin{smallmatrix}COOR\\SO_2OR\\NO_2\end{smallmatrix}$; and consequently, in the chloride of (*p*)-nitro-sulpho-benzoic acid one chlorine atom is in combination with carbon, the other with sulphur, as represented in this formula,

$$C_6H_3\begin{smallmatrix}COCl\ (1)\\SO_2Cl\ (2)\\NO_2\ (4)\end{smallmatrix}.$$

The easy formation of nitro-benzoic sulphinide from this chloride

[1] Ber. d. chem. Gesell. **13**, 417. [2] Ber. d. chem. Gesell. **16**, 860. [3] This Journal **3**, 26.

by treatment either with aqueous or gaseous ammonia also speaks strongly in favor of this view.

The results obtained also show that (*p*)-nitro-sulpho-benzoic acid exhibits in a striking way the combined properties of both a sulphonic and a carbonic acid. And finally, from the study of the acid and its derivatives I have been led independently to the same view regarding the structure of the sulphinides as that first proposed by Remsen[1] in 1879, and shown to be correct by Fahlberg and Brackett in 1887.

Paranitro-sulpho-benzoic Acid, $C_6H_3\begin{cases}COOH\ (1)\\SO_2OH\ (2)\\NO_2\ (4)\end{cases}$.—The salts of this acid were first made and studied by Hart,[2] and were obtained by oxidising the calcium salt of nitro-toluene-sulphonic acid with potassium permanganate. The yield obtained by following Hart's directions was so small that I endeavored to find a better method for effecting the oxidation.

It was found advantageous to use the potassium salt of paranitro-toluene-sulphonic acid instead of the calcium salt; and, after a large number of experiments, the following method was found to give the best results:

Ten parts by weight of the potassium salt of (*p*)-nitro-toluene-sulphonic acid, together with 3 parts by weight of potassium hydroxide, are dissolved in 500 parts of water; the balloon-flask containing this solution is then placed on the water-bath, and when it has acquired the temperature of the bath, 22 parts by weight of potassium permanganate are added, and the mixture heated until the color of the permanganate has entirely disappeared. The amber-colored liquid is then filtered from the manganese hydrate, and the dark brown residue thoroughly washed with hot water. The filtrate and washings are then neutralised with hydrochloric acid, and evaporated until the neutral potassium salt begins to crystallise out, when a small quantity of the solution is cooled. The whole of the solution is then allowed to cool, and strong hydrochloric acid added in excess, when the acid potassium salt of paranitro-sulpho-benzoic acid separates out in beautiful fine white needles.

The following results show the excellent yield which it is possible to obtain by following these directions:

1st experiment, 10 grams potassium *p*-nitro-toluene-sulphonate

[1] This Journal **1**, 429. [2] Ibid. **1**, 340.

gave 9.5 grams acid potassium nitro-sulpho-benzoate; 2d experiment, 10 grams gave 9.4 grams; 3d experiment, 50 grams gave 48 grams; 4th experiment, 250 grams gave 240 grams.

When the barium salt of (*p*)-nitro-sulpho-benzoic acid is dissolved in water which has been acidulated with hydrochloric acid, and the barium precipitated by sulphuric acid, a solution of (*p*)-nitro-sulpho-benzoic acid is obtained. This, when evaporated to a small bulk and allowed to cool, yields crystals of the free acid. The acid is very readily soluble in hot water, much less so in cold, and separates from a hot concentrated solution on cooling in beautiful white needles. These melt at 110° C. to a jelly-like mass which does not become perfectly liquid until a considerably higher temperature is reached.

Action of Phosphorus Pentachloride on Acid Potassium (p)-nitro-sulpho-benzoate.

When the acid potassium salt of (*p*)-nitro-sulpho-benzoic acid is intimately mixed with a little more than an equal weight of phosphorus pentachloride, and the mixture heated on the oil-bath to 150° C., reaction takes place with the formation of an acid chloride; phosphorus oxychloride is also formed, and hydrochloric acid is given off—a reaction which is expressed by this equation:

$$C_6H_3\begin{cases}\diagup COOK\\ \diagdown NO_2\end{cases}SO_3OH + 2PCl_5 = C_6H_3\begin{cases}\diagup COCl\\ \diagdown NO_2\end{cases}SO_2Cl + 2POCl_3 + KCl + HCl.$$

The phosphorus oxychloride is distilled off, and there remains in the flask an acid chloride of a wax-like consistency, together with a small quantity of potassium chloride. The acid chloride is then washed with water in order to remove the last traces of the oxychloride and the potassium chloride. It is then separated as completely as possible from the water by means of a separating funnel, and dried over sulphuric acid. Prepared in this way, it is a yellow, wax-like solid, which on long standing over sulphuric acid becomes somewhat granular and crystalline.

It is slightly soluble in petroleum ether, and very readily soluble in chloroform and anhydrous ether. From the latter solvent it crystallises in fine yellow needles or in flat plates which are somewhat elongated. These crystals become waxy on heating, and at 60° they melt to a clear liquid which, on cooling, solidifies. The chloride cannot be distilled; on heating to boiling it decomposes. A chlorine determination, made by dissolving the chloride in

dilute caustic potash and precipitating with silver nitrate, gave the following results:

1.1956 grams of the chloride gave 1.1658 grams AgCl.

0.5089 gram of the chloride gave 0.5052 gram AgCl.

	Calculated for $C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases}$.	Found.
Cl	24.95 per cent.	24.11 per cent. 24.56 "

Action of Ammonia on the Chloride of (p)-nitro-sulpho-benzoic Acid.

When the chloride of (*p*)-nitro-sulpho-benzoic acid is treated with aqueous ammonia, a lively reaction takes place, and the ammonium salt of nitro-benzoic sulphinide is obtained. It is probable that the reaction takes place in this way:

$$C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases} + 4NH_4OH =$$

$$C_6H_3\begin{cases}CO\\SO_2\end{cases}>NH.NH_3 + 2NH_4Cl + 4H_2O.$$
$$\quad NO_2$$

When the perfectly dry chloride is treated with dry ammonia gas, the ammonium salt of nitro-benzoic sulphinide is obtained, together with ammonium chloride; and the same result is reached by treating a solution of the chloride in anhydrous ether with gaseous ammonia. This reaction may be represented thus:

$$C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases} + 2NH_3 = C_6H_3\begin{cases}CONH_2\\SO_2NH_2\\NO_2\end{cases} + 2HCl,$$

$$C_6H_3\begin{cases}CONH_2\\SO_2NH_2\\NO_2\end{cases} + 2HCl + 2NH_3 = C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.NH_4 + 2NH_4Cl.$$

Action of Alcohols on the Chloride of (p)-nitro-sulpho-benzoic Acid.

The chloride of (*p*)-nitro-sulpho-benzoic acid dissolves readily in alcohol with a considerable evolution of heat, and from this solution, on cooling and standing for some time, there is deposited a quantity of white needle-shaped crystals, which were found to have the composition and structure represented by this formula,

$$C_6H_3\begin{cases}COOC_2H_5 & (1)\\SO_2Cl & (2).\\NO_2 & (4)\end{cases}$$

Absolute alcohol acts on the chloride according to this equation,

$$C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases} + HOC_2H_5 = C_6H_3\begin{cases}COOC_2H_5\\SO_2Cl\\NO_2\end{cases} + HCl.$$

When the chloride of (*p*)-nitro-sulpho-benzoic acid is boiled with absolute alcohol, another reaction takes place, and we have as the end-product of the reaction the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid, $C_6H_3\begin{cases}COOC_2H_5\\SO_2OH\\NO_2\end{cases}$; and from certain studies which I have made on the saponification of the *mixed* ethers of (*p*)-nitro-sulpho-benzoic acid, it would seem that the formation of an acid ether from the chloride could be best represented by the following equations:

$$C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases} + 2C_2H_5OH = C_6H_3\begin{cases}COOC_2H_5\\SO_2OC_2H_5\\NO_2\end{cases} + 2HCl,$$

$$C_6H_3\begin{cases}COOC_2H_5\\SO_2OC_2H_5\\NO_2\end{cases} + C_2H_5OH = C_6H_3\begin{cases}COOC_2H_5\\SO_2OH\\NO_2\end{cases} + (C_2H_5)_2O.$$

This reaction of the chloride of (*p*)-nitro-sulpho-benzoic acid with absolute alcohol has been found to be a general one, and it is only necessary to bring together this chloride with any primary alcohol to obtain the corresponding acid ether of (*p*)-nitro-sulpho-benzoic acid, or its acid chloride. As to which of these reactions will take place depends mainly on the temperature at which it is conducted.

Chloride of the Acid Methyl Ether of (*p*)*-nitro-sulpho-benzoic Acid,* $C_6H_3\begin{cases}COOCH_3\ (1)\\SO_2Cl\ (2)\\NO_2\ (4)\end{cases}$.—When the chloride of (*p*)-nitro-sulpho-benzoic acid is dissolved in methyl alcohol and the solution kept cool, there separates out, after a time, a white crystalline compound; the addition of a small quantity of cold water facilitates the separation. This compound is insoluble in cold water, and is soluble in hot water with decomposition.

It is soluble to some extent in cold alcohol, quite readily so in boiling alcohol, from which it separates, on cooling, in fine white needles which melt at 90° C. When the alcoholic solution is boiled for a long time, the compound is decomposed, and there is found

in the solution hydrochloric acid and the acid methyl ether of (*p*)-nitro-sulpho-benzoic acid.

The compound is easily soluble in anhydrous ether, from which it crystallises on slow evaporation in flat, transparent crystals of a prismatic habit. A determination of the chlorine, made by decomposing the compound in dilute alkali and precipitating with silver nitrate, gave the following result:

0.3692 gram of the chloride gave .1925 gram AgCl.

	Calculated for $C_6H_3\begin{cases}COOCH_3\\SO_2Cl\\NO_2\end{cases}$.	Found.
Cl	12.70 per cent.	12.95 per cent.

Chloride of the Acid Ethyl Ether of (p)-nitro-sulpho-benzoic Acid, $C_6H_3\begin{cases}COOC_2H_5 & (1)\\SO_2Cl & (2)\\NO_2 & (4)\end{cases}$.—This compound is obtained by dissolving the chloride of (*p*)-nitro-sulpho-benzoic acid in absolute alcohol, care being taken to keep the solution cool.

It separates out of the alcoholic solution on standing, but the separation is greatly hastened by the addition of a small quantity of water. This compound, like the corresponding methyl compound, is insoluble in cold water, and readily decomposed by boiling water; the products of the decomposition being hydrochloric acid and the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid.

It is easily soluble in hot alcohol, from which it crystallises, on cooling, in fine white needles; it is also easily soluble in anhydrous ether, from which it crystallises, on slow evaporation, in large, well defined crystals of a prismatic habit. These are transparent and have a high lustre, and were found to belong to the monoclinic system. The substance melts at 67°–68° C. uncorrected, to a clear oily liquid which, on cooling, again solidifies.

The compound gave the following figures on analysis:

0.2471 gram of the chloride gave 0.1237 gram AgCl.

0.2419 gram of the chloride gave 0.1966 gram $BaSO_4$.

	Calculated for $C_6H_3\begin{cases}COOC_2H_5\\SO_2Cl\\NO_2\end{cases}$.	Found.
S	10.90 per cent.	11.12 per cent.
Cl	12.09 "	12.30 "
N	4.77 "	4.41 " 4.70 "

Chloride of the Acid Propyl Ether of (p)-nitro-sulpho-benzoic Acid, $C_6H_3\begin{cases}COOC_3H_7\ (1)\\SO_2Cl\ (2)\\NO_2\ (4)\end{cases}$.—About five grams of the chloride of (*p*)-nitro-sulpho-benzoic acid were dissolved in about 30 cc. of normal propyl alcohol, and the solution allowed to evaporate spontaneously. A substance crystallised out in white leaflets which was found to react in the same way as the ethyl compound just described. Although no analysis was made of this compound, there can be little doubt that it is made up in the manner represented above.

Action of Water on the Chloride of the Acid Ethyl Ether of (p)-nitro-sulpho-benzoic Acid.

When this compound is boiled for some time with water it dissolves completely and an intensely acid liquid results. This acid solution was neutralised with barium carbonate, filtered, and the filtrate evaporated to one half its original bulk. On cooling, a barium salt crystallised out which was found to be identical in every way with the barium salt of the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid (see p. 190).

It gave the following figures on analysis:

0.2127 gram of the salt lost on heating to 150° 0.0203 gram.

0.1924 gram of the dried salt gave 0.0654 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}COOC_2H_5\\SO_3O\\NO_2\end{cases}\right)_2 Ba + 4H_2O$.	Found.
H_2O	9.51 per cent.	9.54 per cent.
	Calculated for the dried salt.	
Ba	20 per cent.	19.95 per cent.

The acid solution obtained in this experiment was also found to contain a considerable quantity of hydrochloric acid, and the action of the water on this compound can be best understood by this equation,

$$C_6H_3\begin{cases}COOC_2H_5\\SO_2Cl\\NO_2\end{cases} + H_2O = C_6H_3\begin{cases}COOC_2H_5\\SO_2OH\\NO_2\end{cases} + HCl.$$

Action of Alcoholic Ammonia on the Chloride of the Acid Ethyl Ether of (p)-nitro-sulpho-benzoic Acid.

About five grams of the chloride were dissolved in about 50 cc. of a saturated alcoholic solution of ammonia; the solution was then heated on the water-bath under pressure for about an hour.

The solution thus obtained was evaporated on the water-bath, and the residue dissolved in hot water; on cooling, a substance crystallised out in thin leaflets having a sweet-bitter taste resembling that of nitro-benzoic sulphinide.

This substance was again dissolved in water, and a few drops of strong hydrochloric acid added, when a substance crystallised out in fine yellowish needles which were found to melt at 208°–209° C. uncorrected. In order to make sure that nitro-benzoic sulphinide had been formed in this experiment, the crystals melting at 208°–209° C. were dissolved in strong ammonia and reduced with sulphuretted hydrogen. The product of the reduction proved to be the amido-benzoic sulphinide, which was recognised by its intensely sweet taste, its fluorescent solution, and its melting point (284°–285° C.).

Action of Aqueous Ammonia on the Chloride.

About 10 grams of the chloride were boiled with strong aqueous ammonia under a reflux condenser. When the chloride had completely dissolved, a portion of the liquid was distilled off. The distillate was neutralised with dilute sulphuric acid and redistilled. The distillate obtained was treated with dilute alkali and iodine, when a precipitate of iodoform was produced, thus proving that alcohol had been formed in the reaction.

The residue from the first distillation was found to contain the ammonium salt of nitro-benzoic sulphinide. This reaction is, I think, one of the strongest arguments in favor of the formula $R<\begin{matrix}CO\\SO_2\end{matrix}>NH$ as correctly representing the constitution of the sulphinides. It will be shown that the chloride of the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid has, in all probability, the structure represented by this formula, $C_6H_3\begin{matrix}\diagup COOC_2H_5 & (1)\\ -SO_2Cl & (2)\\ \diagdown NO_2 & (4)\end{matrix}$, and consequently the action of aqueous ammonia can be best explained by this equation,

$$C_6H_3\begin{matrix}\diagup COOC_2H_5\\ -SO_2Cl\\ \diagdown NO_2\end{matrix} + 3NH_4OH =$$

$$C_6H_3\begin{matrix}\diagup CO\\ -SO_2>N.NH_4\\ \diagdown NO_2 + H_2O\end{matrix} + C_2H_5OH + NH_4Cl.$$

When perfectly dry ammonia gas is passed over the dry chloride which has been slightly warmed, quite a lively reaction takes place. Ammonium chloride is formed in considerable quantity, and on treating the mass which remains after the reaction with water, there is obtained, together with a large quantity of the ammonium salt of nitro-benzoic sulphinide, a small quantity of a substance which is soluble with difficulty even in hot water, and which crystallises from dilute alcohol in radial tufts of fine white needles. This substance melts at 141° C. uncorrected, and from its method of formation is probably to be represented by the formula $C_6H_3\begin{cases}COOC_2H_5\\SO_2NH_2\\NO_2\end{cases}$, although it was not obtained in sufficient quantity for analysis.

Action of Alcohol on the Chloride of the Acid Ethyl Ether of (p)-nitro-sulpho-benzoic Acid.

A few grams of the chloride were heated with absolute alcohol in a pressure bottle in a water-bath, in the hope of obtaining the di-ethyl ether of (*p*)-nitro-sulpho-benzoic acid. After heating for about an hour, the resulting alcoholic solution was evaporated on the water-bath. Instead of obtaining a neutral ether, an intensely acid syrup was thus obtained, which became somewhat crystalline on cooling. This was dissolved in a large quantity of water and neutralised with barium carbonate. On concentrating the solution, a barium salt crystallised out in fine white needles having the appearance and properties of the barium salt of the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid described on page 190.

It gave the following numbers on analysis:

0.2714 gram of the salt lost on heating to 150° C. 0.0257 gram.

0.2457 gram of the dried salt gave 0.0841 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}COOC_2H_5\\SO_3O\\NO_2\end{cases}\right)_2Ba + 4H_2O$.	Found.
H_2O	9.51 per cent.	9.47 per cent.
	Calculated for the dried salt.	
Ba	20 per cent.	20.10 per cent.

From a study of the saponification of the ethers of (*p*)-nitro-sulpho-benzoic acid, it seems highly probable that this reaction takes place thus:

$$C_6H_3\begin{cases}COOC_2H_5\\SO_2Cl\\NO_2\end{cases} + C_2H_5OH = C_6H_3\begin{cases}COOC_2H_5\\SO_2OC_2H_5\\NO_2\end{cases} + HCl,$$

$$C_6H_3\begin{cases}COOC_2H_5\\SO_2OC_2H_5\\NO_2\end{cases} + C_2H_5OH = C_6H_3\begin{cases}COOC_2H_5\\SO_2OH\\NO_2\end{cases} + (C_2H_5)_2O.$$

Acid Ethers of (*p*)-nitro-sulpho-benzoic Acid and some of their Salts.

Acid Methyl Ether of (*p*)*-nitro-sulpho-benzoic Acid*, $C_6H_3\begin{cases}COOCH_3\\SO_2OH\\NO_2\end{cases}$.—When the chloride of (*p*)-nitro-sulpho-benzoic acid is dissolved in methyl alcohol, and this solution heated on the water-bath under an inverted condenser for about three hours, there separates out, on cooling, a quantity of beautiful fine white needles, which have a strong acid taste and reaction, and when dissolved in water the substance decomposes carbonates with ease.

The acid is difficultly soluble in methyl alcohol, very easily soluble in water, crystallising out of a very concentrated aqueous solution in fine white needles which show a strong tendency to concentric grouping. When heated, these crystals begin to blacken at 212°–215° C., and melt with decomposition at 270° C.

This acid forms stable, well defined salts, most of which have a strong crystallising power. The following salts have been made and studied:

Barium Methyl-(*p*)*-nitro-sulpho-benzoate*, $\left(C_6H_3\begin{cases}COOCH_3\\SO_2O\\NO_2\end{cases}\right)_2 Ba + 3H_2O$.—This salt was made by neutralising the acid ether just described with barium carbonate. The salt crystallises in flat shining plates, or in yellow needles, and it is easily soluble in hot water; less soluble in cold.

The water of crystallisation and the barium were determined, with following results:

0.2103 gram of the salt lost on heating to 150° 0.0162 gram.

0.1941 gram of the dried salt gave 0.0689 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}COOCH_3\\SO_2O\\NO_2\end{cases}\right)_2 Ba + 3H_2O$.	Found.
H_2O	7.59 per cent.	7.75 per cent.
	Calculated for the dried salt.	
Ba	20.85 per cent.	20.90 per cent.

Calcium Methyl-(p)-nitro-sulpho-benzoate, $\left(C_6H_3\begin{cases}\diagup COOCH_3\\ -SO_2O\\ \diagdown NO_2\end{cases}\right)_2 Ca + 3H_2O$.—This salt was made by neutralising the free acid with precipitated chalk. The salt is very easily soluble in hot and cold water, and crystallises from a very concentrated solution in fine white needles which have a satiny lustre.

An analysis gave the following numbers:

0.2242 gram of the salt lost on heating to 140° 0.0182 gram.

0.2260 gram of the dry salt gave 0.0567 gram $CaSO_4$.

Calculated for $\left(C_6H_3\begin{cases}\diagup COOCH_3\\ -SO_2O\\ \diagdown NO_2\end{cases}\right)_2 Ca + 3H_2O$.		Found.
H_2O	8.79 per cent.	8.11 per cent.

Calculated for $\left(C_6H_3\begin{cases}\diagup COOCH_3\\ -SO_2O\\ \diagdown NO_2\end{cases}\right)_2 Ca$.		Found.
Ca	7.14 per cent.	7.34 per cent.

Potassium Methyl-(p)-nitro-sulpho-benzoate, $C_6H_3\begin{cases}\diagup COOCH_3\\ -SO_2OK\\ \diagdown NO_2\end{cases}$.—This salt was made by neutralising the free acid with pure potassium carbonate. From a hot aqueous solution the salt separates out, on cooling, in beautiful white plates which show a beautiful iridescence, and resemble potassium chlorate in their general appearance. Under other conditions, however, when the salt has been allowed to crystallise slowly, it has been obtained in crystals of good size. Some of these crystals have been measured and studied by Mr. A. C. Gill.

The results of his measurements are as follows: The crystals are triclinic, having a perfect cleavage in the plane assumed as the base.

Five specimens having moderately good reflecting surfaces gave the following mean result: $\breve{a} : \bar{b} : c' = .6314 : 1 : .7104$. The angles between the pinacoids are as follows:

OP to $\infty P\bar{\infty}$, 58° 0′ 40″; OP to $\infty P\breve{\infty}$, 93° 27′ 30″; $\infty P\bar{\infty}$ to $\infty P\breve{\infty}$, 79° 20.

The development of the form P′ was very variable; on most of the crystals, especially the smaller ones, slight.

An analysis of the salt gave the following result:

0.2208 gram of the salt lost on heating to 175° 0.0003 gram.

0.2205 gram of the dried salt gave 0.0645 gram K_2SO_4.

Calculated for $C_6H_3\begin{cases}COOCH_3\\SO_2OK\\NO_2\end{cases}$.		Found.
K	13.18 per cent.	13.10 per cent.

Sodium Methyl-(p)-nitro-sulpho-benzoate,

$C_6H_3\begin{cases}COOCH_3\\SO_2ONa\\NO_2\end{cases} + H_2O$.—This salt was made from the calcium salt by treating a hot solution of the calcium salt with sodium carbonate. It is easily soluble in hot water, soluble with difficulty in the cold, and separates, when the hot solution is allowed to cool, in small white needles, sometimes in flat transparent plates.

0.2792 gram of the salt, when dried at 175°, lost 0.0142 gram.

0.2650 gram of the dried salt gave 0.0680 gram Na_2SO_4.

Calculated for $C_6H_3\begin{cases}COOCH_3\\SO_2ONa\\NO_2\end{cases} + H_2O$.		Found.
H_2O	5.98 per cent.	5.08 per cent.

Calculated for $C_6H_3\begin{cases}COOCH_3\\SO_2ONa\\NO_2\end{cases}$.		Found.
Na	8.12 per cent.	8.30 per cent.

Copper Methyl-(p)-nitro-sulpho-benzoate,

$\left(C_6H_3\begin{cases}COOCH_3\\SO_2O\\NO_2\end{cases}\right)_2 Cu + 8H_2O$.—This salt was made by treating the barium salt with an equivalent amount of copper sulphate. The barium sulphate was filtered off and the green solution evaporated to a small bulk, when the copper salt crystallised out in thin leaflets showing a tendency to concentric grouping.

When perfectly dry the salt has a most beautiful apple-green color, together with a pearly lustre. It is easily soluble in hot and cold water. On being heated, the salt loses its water of crystallisation and becomes colorless.

An analysis gives the following numbers:

0.2080 gram of the salt lost 0.0412 gram when dried at 180° C.

0.1668 gram of the dried salt gave 0.0177 gram Cu.

Calculated for $\left(C_6H_3\begin{cases}COOCH_3\\SO_2O\\NO_2\end{cases}\right)_2 Cu + 8H_2O$.		Found.
H_2O	19.80 per cent.	19.80 per cent.

	Calculated for $C_6H_3\begin{matrix}/COOCH_3\\ \\ \backslash NO_2\end{matrix}—SO_2O\,Cu$.	
Cu	10.80 per cent.	10.61 per cent.

When a concentrated aqueous solution of the copper salt is treated with strong ammonia, a beautiful cupr-ammonium compound is formed which separates from the solution in dark blue needles.

Silver Methyl-(p)-nitro-sulpho-benzoate, $C_6H_3\begin{matrix}/COOCH_3\\ —SO_3OAg\ (?).—\\ \backslash NO_2\end{matrix}$

When an aqueous solution of the acid methyl ether is treated with freshly precipitated silver carbonate, and the solution, filtered from excess of silver carbonate, evaporated to dryness on the water-bath, the silver salt of the acid methyl ether is obtained. On account of its great solubility and the ease with which it is blackened on exposure to light, no analysis was attempted, but from its reaction with ethyl iodide, there can be little doubt that the anhydrous salt has the composition $C_6H_3\begin{matrix}/COOCH_3\\ —SO_2OAg.\\ \backslash NO_2\end{matrix}$

Acid Ethyl Ether of (p)-nitro-sulpho-benzoic Acid,

$C_6H_3\begin{matrix}/COOC_2H_5\ (1)\\ —SO_2OH\ \ (2).\\ \backslash NO_2\ \ \ (4)\end{matrix}$—This acid is most easily made by boiling about 10 parts by weight of the chloride of (*p*)-nitro-sulpho-benzoic acid with 25 parts by weight of absolute alcohol. The excess of alcohol is evaporated off, and there remains a thick syrup which, on standing, becomes crystalline.

Like the corresponding methyl compound, this acid crystallises from dilute alcohol in fine white needles which blacken at a high temperature. The acid ethyl ether is a strong acid, and forms salts which crystallise well.

The following have been made and analysed:

Barium Ethyl-(p)-nitro-sulpho-benzoate,

$\left(C_6H_3\begin{matrix}/COOC_2H_5\\ —SO_2O\\ \backslash NO_2\end{matrix}\right)_2 Ba + 4H_2O$.—The free acid was neutralised with barium carbonate, the hot solution was filtered from the excess of carbonate and allowed to cool, when the barium salt crystallised out in long white needles which show a strong tendency to concentric grouping.

It is easily soluble in hot water, and is but slightly soluble in the cold. The following is the result of analysis:

0.2366 gram of the salt lost on heating to 175° C. 0.0225 gram.

0.2141 gram of the dried salt gave 0.0734 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}COOC_2H_5\\SO_3O\\NO_2\end{cases}\right)_2Ba + 4H_2O$.	Found.
H_2O	9.51 per cent.	9.50 per cent.
	Calculated for the dried salt.	Found.
Ba	20 per cent.	20.14 per cent.

Potassium Ethyl-(p)-nitro-sulpho-benzoate, $C_6H_3\begin{cases}COOC_2H_5\\SO_3OK\\NO_2\end{cases} + H_2O$.—This salt can easily be obtained by neutralising the free acid with potassium carbonate. It is easily soluble in hot water, less so in cold. An analysis gave the following numbers:

0.2569 gram of the salt lost on heating to 140° C. 0.0138 gram.

0.2431 gram of the dried salt gave 0.0681 gram K_2SO_4.

	Calculated for $C_6H_3\begin{cases}COOC_2H_5\\SO_3OK\\NO_2\end{cases} + H_2O$.	Found.
H_2O	5.42 per cent.	5.33 per cent.
	Calculated for $C_6H_3\begin{cases}COOC_2H_5\\SO_3OK\\NO_2\end{cases}$.	Found.
K	12.59 per cent.	12.62 per cent.

Copper Ethyl-(p)-nitro-sulpho-benzoate.—The copper salt of the acid ethyl ether can be best made by treating the barium salt with an equivalent quantity of copper sulphate. It is very soluble, and crystallises after long standing in light green leaflets, and, like the copper salt of the acid methyl ether, it forms a beautiful cupr-ammonium compound when treated with strong ammonia.

Silver Ethyl-(p)-nitro-sulpho-benzoate.—This salt has been prepared in considerable quantity by neutralising the aqueous solution of the acid ethyl ether with freshly precipitated silver carbonate. The excess of silver carbonate is filtered off and the filtrate evaporated to dryness on the water-bath. The silver salt thus obtained is very soluble; on long standing in the dark it crystallises from water in fine silken needles. It blackens on exposure to light, and on this account was not analysed.

The acid ethers of (*p*)-nitro-sulpho-benzoic acid can also be prepared by treating the free acid with a primary alcohol and hydrochloric acid gas.

ETHERS AND MIXED ETHERS OF (*p*)-NITRO-SULPHO-BENZOIC ACID.

Di-ethyl (p)-nitro-sulpho-benzoate, $C_6H_3\begin{cases}COOC_2H_5 & (1)\\ SO_3OC_2H_5 & (2)\\ NO_2 & (4)\end{cases}$.—The dry silver salt of the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid was heated to 100° C. with ethyl iodide for two hours. The pressure bottle in which the reaction had been carried on was then allowed to cool and the contents extracted with 95 per cent. alcohol.[1] The extract was filtered hot and allowed to stand, when a substance crystallised out in thin white leaflets. The substance thus obtained is but slightly soluble in cold alcohol, easily soluble in hot alcohol. The substance shows a strong crystallising power. When pure it crystallises from alcohol in leaflets of a very beautiful pearly lustre. It is precipitated from its alcoholic solution by water, in which it is insoluble. When heated with water it melts to a clear, heavy oil which solidifies again when the water becomes cold. It also dissolves quite readily in ether, from which it separates on slow evaporation in bright, transparent crystals.

The thin leaflets obtained from alcohol were found to melt at 65°–66° C. uncorrected.

A determination of the sulphur in the compound was made by Liebig's method, with the following result:

0.1893 gram of the ether gave 0.1464 gram $BaSO_4$.

	Calculated for $C_6H_3\begin{cases}COOC_2H_5\\ SO_3OC_2H_5\\ NO_2\end{cases}$.	Found.
S	10.56 per cent.	10.61 per cent.

Action of Ammonia on the Di-ethyl Ether.

About 5 grams of the ether were dissolved in a concentrated alcoholic solution of ammonia, and the solution heated to 100° C. in a pressure bottle for about an hour. A compound readily soluble in water was obtained in this way, which, on standing over sulphuric acid, crystallised from its aqueous solution in large, trans-

[1] It has since been found better to use absolute ether for the extraction.

parent, tabular plates. The substance was found to dissolve in a solution of caustic potash with liberation of ammonia, even in the cold, and on heating this alkaline solution and evaporating, the neutral potassium salt of (*p*)-nitro-sulpho-benzoic acid crystallised out.

These crystals were dissolved in a small quantity of water, and a drop or two of strong hydrochloric acid added, when the characteristic acid potassium salt of (*p*)-nitro-sulpho-benzoic acid crystallised out in fine white needles.

From this it seems that the action of ammonia on the ether is simply that of saponification.

Action of Water on the Di-ethyl Ether.

About 2 grams of the ether were boiled with distilled water for about an hour; at the end of that time the resulting acid liquid was neutralised with barium carbonate. The solution was filtered from the excess of barium carbonate and evaporated. On cooling, the barium salt of the acid ethyl ether crystallised out. This salt gave the following numbers on analysis, and was found to be identical in every respect with the salt described on p. 190:

	Found.
Ba	20.09 per cent.
H_2O	9.60 "

Action of Alcohol on the Di-ethyl Ether.

1 gram of the di-ethyl ether was dissolved in absolute alcohol, and the solution heated to 100° C. in a pressure bottle for about an hour. At the end of that time the alcohol was evaporated off, and the acid syrup thus obtained dissolved in water and neutralised with barium carbonate.

The barium salt thus obtained was found, like the one just described, to be the barium salt of the acid ethyl ether,

$$\left(C_6H_3\begin{cases}COOC_2H_5\\SO_2O\\NO_2\end{cases}\right)_2Ba.$$

This easy saponification of one of the ether residues by one equivalent of alkali, by water and by alcohol, is very interesting, and is characteristic of all the ethers of (*p*)-nitro-sulpho-benzoic acid, and is, as I shall soon show, a reaction which affords the best experimental evidence of the correctness of the views expressed concerning their constitution.

Ethyl-methyl (p)-nitro-sulpho-benzoate, $C_6H_3\begin{cases}COOC_2H_5\ (1)\\ SO_2OCH_3\ (2).\\ NO_2\ (4)\end{cases}$—

The silver salt of acid ethyl-(*p*)-nitro-sulpho-benzoate was treated with the calculated amount of methyl iodide. When these substances were brought together in this proportion, reaction took place at once, with the formation of silver iodide and the ethyl-methyl ether. In order to insure its completion, however, the pressure bottle in which these two substances had been brought together was heated on the water-bath for half an hour.

The contents of the pressure bottle were then extracted with anhydrous ether, the extract filtered and allowed to evaporate slowly, when the ethyl-methyl ether crystallised out. This compound, like the di-ethyl ether, is insoluble in water. It is easily soluble in alcohol, from which it crystallises in short, thick, rounded white crystals. It is easily soluble in ether, from which it crystallises in flat, slightly elongated, transparent prisms. After several recrystallisations from alcohol the ether melted at 80° C. (uncorrected) to a clear liquid, which solidified again at 65° C.

The sulphur was determined by Liebig's method, with the following result:

0.2051 gram substance gave 0.1682 gram $BaSO_4$.

	Calculated for $C_6H_3\begin{cases}COOC_2H_5\\ SO_2OCH_3.\\ NO_2\end{cases}$	Found.
S	11.07 per cent.	11.26 per cent.

Experiments on the saponification of the ethyl-methyl ether were made with the view of determining which alkyl group remained in the compound and which was split off.

Action of Caustic Potash on the Ethyl-methyl Ether.

About 1 gram of the ether was treated with dilute caustic potash, in the proportion of 1 molecule to 1 molecule of the ether. The saponification took place easily, and a quantitative yield of a potassium salt was obtained which gave the following numbers on analysis:

0.2120 gram salt lost on heating to 140° C. 0.0116 gram.

0.2004 gram dried salt gave 0.0561 gram K_2SO_4.

	Found.
H_2O	5.47 per cent.
K	12.87

These figures agree sufficiently well with those calculated for the potassium salt of the acid ethyl ether. (See p. 191.)

Action of Water on the Ethyl-methyl Ether.

When the ethyl-methyl ether is heated with distilled water it first melts to a clear heavy oil which, after long boiling and considerable agitation, goes into solution. The solution, which now reacts acid, is neutralised with barium carbonate, filtered and evaporated, when the characteristic barium salt of the acid ethyl ether crystallises out.

Action of Alcohol on the Ethyl-methyl Ether.

Hot absolute alcohol readily dissolves the ethyl-methyl ether, and when this solution was heated in a pressure bottle for about an hour at the temperature of the water-bath, the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid was formed. This was proved by neutralising the acid liquid with barium carbonate, and analysing the barium salt thus formed.

From these experiments it is clear that the ethyl group is the one which is held most firmly in the compound, inasmuch as the acid ethyl ether is obtained when the mixed ether is treated with one equivalent of caustic potash, or with even such mild saponifying agents as water and alcohol.

Methyl-ethyl (*p*)*-nitro-sulpho-benzoate*, $C_6H_3\begin{cases}\diagup COOCH_3 & (1)\\ -SO_3OC_2H_5 & (2)\\ \diagdown NO_2 & (4)\end{cases}$.

—The silver salt of acid methyl-(*p*)-nitro-sulpho-benzoate was treated with ethyl iodide in a pressure bottle at the temperature of the water-bath, in the proportion of 1 mol. of the silver salt to 1 mol. of the iodide. The reaction took place readily, with abundant formation of silver iodide. After an hour's heating, the contents of the bottle were extracted with anhydrous ether, the extract filtered and allowed to evaporate, when the methyl-ethyl ether was obtained.

Like its isomer, and like the di-ethyl ether, it is insoluble in cold water, it melts to a clear oil when the water is heated, and is slowly decomposed into alcohol and the acid methyl ether, both of which pass into solution. It is easily soluble in hot alcohol, less so in cold, so that on cooling it separates from the hot concentrated alcoholic solution in clusters of fine white needles. In this respect it differs

from its isomer, which always crystallises from alcohol in short compact crystals, and never in needles. It is also easily soluble in ether, from which it crystallises in fine white needles which, when pure, were found to melt at 68° C. uncorrected. A sulphur determination by Liebig's method gave the following result:

0.2189 gram of substance gave 0.1772 gram $BaSO_4$.

	Calculated for $C_6H_3\begin{cases}COOCH_3\\SO_3OC_2H_5\\NO_2\end{cases}$.	Found.
S	11.07 per cent.	11.10 per cent.

Action of Water on the Methyl-ethyl Ether.

When the methyl-ethyl ether is heated with distilled water, it first melts to a clear heavy oil which, on continued shaking, passes into solution. This solution was found to react acid, and was accordingly neutralised with barium carbonate, when a barium salt identical with the one described on page 187 was obtained.

	Found.
H_2O	7.9 per cent.
Ba	20.7

These figures agree sufficiently well with those required by the salt above referred to.

Action of Absolute Alcohol on the Methyl-ethyl Ether.

About 5 grams of the ether were dissolved in absolute alcohol, and the solution heated in a pressure bottle at 100° C. for an hour. At the end of that time the solution was found to react acid, and was neutralised with barium carbonate. The barium salt of the acid methyl ether was obtained. This easy saponification of one of the ether residues in these mixed ethers by one equivalent of caustic potash, by water and even by alcohol, with the production of the acid ethyl ether from the one, and the acid methyl ether from the other, exhibits in a striking way the character of the isomerism which is here presented, and shows clearly that in the compound first described, viz. the ethyl-methyl ether, $C_6H_3\begin{cases}COOC_2H_5\\SO_2OCH_3\\NO_2\end{cases}$, the methyl group is less firmly held in the molecule than the ethyl, whereas in the other the reverse of this is true.

General Considerations.

The careful study of the saponification phenomena exhibited by these mixed ethers not only shows in a clear way the character of their isomerism, but it has also enabled me to explain the constitution of these and other compounds described in the preceding pages, and to interpret certain reactions which otherwise would scarcely admit of a rational explanation.

It has been shown that when these mixed ethers are treated either with one equivalent of caustic potash, with water or with alcohol, one alkyl group is easily split off, whereas the other remains in the compound, and that an *acid* ether in the place of a *neutral* ether results.

Further, it has been shown that the alkyl group which enters the compound last is the first to leave it when the ether is saponified. This would seem to indicate that in both cases it is in combination with the same acid residue. If this be true, then with what acid residue is it in combination: is it united to the carbonic acid portion or to the sulphonic acid portion of this dibasic acid?

The answer to this question is to be found in the comparative study of the conduct of the ethers of the carbonic and sulphonic acids respectively. It is well known that the ethers of the carbonic acids are stable substances; it is true they can all be saponified by means of the strong alkalies, but with water no reaction takes place, or if it does, it is only to an inappreciable extent.

In the case of the lactones, which may be regarded as ethers of carbonic acids in which the ether formation has taken place in one and the same molecule, water does act as a saponifying agent; but even here this reaction has been shown by Fittig to be a reversible one, and consequently takes place only to a limited extent.

This exception, however, if it is to be regarded as such, is not to the point, inasmuch as the substances here treated of cannot possibly be considered lactones. Towards alcohol the ethers of the carbonic acids are perfectly stable, no reaction whatever taking place when these substances are brought together.

With the ethers of the sulphonic acids, however, the case is entirely different. These substances are not only acted on by strong alkalies with the greatest ease, but they are also easily decomposed by water into the free acid and alcohol. Regarding their conduct towards alcohol I have been unable to find any state-

ments, but when we consider the ease with which alcohol acts on the acid ethers of sulphuric acid it seems highly probable that these substances would undergo similar transformations.

In the light of all this it seems highly probable that in the ethyl-methyl ether described on p. 194 we have the methyl replacing the acid hydrogen of the sulphonic acid portion of the compound, inasmuch as the *acid ethyl ether* is obtained when this compound is treated with water or with alcohol. These facts find their simplest explanation in this formula,

$$C_6H_3\begin{cases}\diagup COOC_2H_5 & (1)\\ -SO_2OCH_3 & (2).\\ \diagdown NO_2 & (4)\end{cases}$$

In the methyl-ethyl ether, on the other hand, we have found that the reverse of this is true; on treating this compound with water, the acid methyl ether was obtained. This decomposition can be most easily explained by means of this formula,

$$C_6H_3\begin{cases}\diagup COOCH_3 & (1)\\ -SO_2OC_2H_5 & (2).\\ \diagdown NO_2 & (4)\end{cases}$$

The formula $C_6H_3\begin{cases}\diagup COOC_2H_5 & (1)\\ -SO_2OC_2H_5 & (2)\\ \diagdown NO_2 & (4)\end{cases}$ for the di-ethyl ether is also

in strict accordance with the facts, inasmuch as it also is partially saponified when treated with water, the acid ethyl ether being the result of the action,

$$C_6H_3\begin{cases}\diagup COOC_2H_5\\ -SO_2OC_2H_5\\ \diagdown NO_2\end{cases} + HOH = C_6H_3\begin{cases}\diagup COOC_2H_5\\ -SO_2OH\\ \diagdown NO_2\end{cases} + C_2H_5OH.$$

From this it is clear that the acid ethers of (*p*)-nitro-sulpho-benzoic acid are to be regarded as made up in this way,

$C_6H_3\begin{cases}\diagup COOR\\ -SO_3OH, \text{ in which R represents any alkyl.}\\ \diagdown NO_2\end{cases}$

This formula for these compounds also finds support in the fact that the acid ethyl ether can be prepared by treating (*p*)-nitro-sulpho-benzoic acid with alcohol and gaseous hydrochloric acid.

The structure of the compounds described on pages 182, 184 also admits of an easy explanation. We have seen from their reactions that, notwithstanding the fact that they possess to some extent the properties of ethereal salts, they are nevertheless to be regarded

as true acid chlorides. The ease with which they pass into the corresponding acid ethers of (*p*)-nitro-sulpho-benzoic acid shows that they must have the constitution represented by this formula,

$$C_6H_3\begin{cases}\diagup COOR\\ —SO_2Cl.\\ \diagdown NO_2\end{cases}$$

The ease with which nitro-benzoic sulphinide is formed from these compounds by treatment with ammonia can easily be explained by the aid of this formula. It is also clear from the reactions which have already been described that the structure of the chloride of (*p*)-nitro-sulpho-benzoic acid can be best represented by this formula,

$$C_6H_3\begin{cases}\diagup COCl & (1)\\ —SO_2Cl & (2).\\ \diagdown NO_2 & (4)\end{cases}$$

That the chlorine atoms in this compound are not held in the same way is evident, inasmuch as but one of them is replaced, and not both, when the chloride is treated with absolute alcohol.

The easy formation of nitro-benzoic sulphinide from the compounds thus prepared, and from the chloride of (*p*)-nitro-sulpho-benzoic acid itself, also finds a simple explanation on the assumption that the formula above given correctly represents the structure of this chloride.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, *March*, 1888.

REVIEWS AND REPORTS.

RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.

2. ALKALI MANUFACTURE.

The most striking change in the alkali industry which the last ten years have witnessed is the rapid growth and extension of the ammonia-soda process. Works have been established by the Solvays in Germany, Austria, Russia, and the United States, and the production of ammonia-soda has rapidly increased, while the

Leblanc-soda industry has steadily declined. Between the years 1880 and 1886 the amount of ammonia-soda produced in the United Kingdom increased from 18,800 tons to 85,000 tons, while the production of Leblanc-soda decreased during the same period from 266,000 tons to 165,782 tons.

A paper by the late Mr. Walter Weldon, read before the Society of Chemical Industry on the eighth of January, 1883,[1] gave a very interesting and complete review of the position in which these two rival processes stood at that time, and stated the probable tendency of the whole alkali industry in the near future. It will be of interest to inquire briefly to what extent these forecasts have been realised.

Mr. Weldon described the failing condition of the Leblanc-soda industry and the threatening attitude of the ammonia process, and stated that soda was then being made by the latter process at a cost fully one pound sterling lower than by the former. Nevertheless he was of the opinion that the Leblanc process would soon be greatly cheapened, and would thus be enabled to hold its own. The economies which he believed would produce this result are, 1st, cheaper pyrites; 2d, cheaper fuel in the form of gas made from waste coal, with recovery of tar and ammonia; and 3d, recovery of sulphur from the alkali-waste.

Within a few months after the presentation of this paper, the Tharsis Company broke away from the combination of Spanish pyrites producers by which the price had been maintained at 6d. per unit of sulphur, and reduced the price to 3d. per unit. It is probable that a still further reduction may be made, and that the Spanish producers are in a position to furnish English sulphuric acid makers with pyrites free of charge, merely stipulating that the cinders shall be returned to be treated for copper. It would, of course, be cheaper to burn the pyrites in Spain, letting the sulphur go to waste, but the great damage to agriculture which this operation has caused in the past has led to the enactment of stringent regulations which will make it impossible to carry on this process on a large scale.

Recovery of Sulphur from Alkali-waste.—The final success of a practical method of recovering the sulphur from tank-waste has been announced during the past year. As this discovery is likely to exert an important influence on the alkali and sulphur industries of the world, it may be of interest to review briefly the history of sulphur recovery.

All the sulphur used in making acid for the alkali industry finally appears at the end of the process, chiefly as calcium sulphide, in the tank-waste. In England there are produced yearly one and one-half million tons of this waste, containing 10 to 14 per

[1] Journal of the Soc. of Chem. Ind. 1883; reprinted in the Amer. Chem. J. Jan. 1883, and Chem. News, Feb. 9, 1883.

cent. of sulphur. This material is not only useless, but it is a source of intolerable nuisance on account of the odors which rise from it and the pollution of the streams which it causes when allowed to accumulate near water-courses. The effective disposal of this immense mass of waste is a great source of expense. Many attempts have been made to extract the sulphur from the material and at the same time render the waste inoffensive. The methods of Schaffner and Mond depend upon the more or less complete oxidation of the waste, and the separation of sulphur from the resulting mixture of calcium sulphide and thiosulphate by treatment with hydrochloric acid. These processes have been used to some extent, especially in Germany, for many years, but resulted in the recovery of not more than half the sulphur of the waste. They cannot be said to have been commercially successful.

Schaffner and Helbig's process, introduced in 1878, was designed to recover all the sulphur in the form of hydrogen sulphide. This is accomplished by heating the waste in tanks with a solution of magnesium chloride, in which operation the following reaction takes place:

$$CaS + MgCl_2 + 2H_2O = CaCl_2 + Mg(OH)_2 + H_2S.$$

By passing carbon dioxide into the resulting solution of calcium chloride containing magnesium hydroxide in suspension, magnesium chloride is regenerated, to be used over again, and calcium carbonate is precipitated in a form well adapted for use in the black ash process:

$$CaCl_2 + Mg(OH)_2 + CO_2 = CaCO_3 + MgCl_2 + H_2O.$$

The hydrogen sulphide given off in the first reaction is in part burned to sulphur dioxide, and this gas brought into contact with the remaining hydrogen sulphide in a solution of calcium chloride; the well known reaction,

$$2H_2S + SO_2 = 3S + 2H_2O$$

takes place. The effect of the calcium chloride is to cause the sulphur to separate in a flocculent form, in which it settles readily, and to prevent the formation of polythionic acids, which would cause loss.

This process was to some extent introduced into England; the production of sulphur by the action of sulphur dioxide and hydrogen sulphide was, however, never satisfactorily carried out in practice, and the recent great reduction in the price of pyrites caused attempts to use the process to be generally abandoned.

Weldon proposed to reduce the amount of magnesium chloride necessary in the first reaction to one-half by employing Krausshaar's process of heating the tank-waste with water under pressure, by which the sulphide is converted into hydrosulphide and hydrate:

$$2CaS + 2H_2O = Ca(SH)_2 + Ca(OH)_2.$$

The calcium hydrate was to be filtered out, and the solution of the hydrosulphide treated with magnesium chloride, of which only one equivalent would be required to two of hydrogen sulphide obtained; the magnesium hydrate, being free from the impurities of the tank-waste, would be a salable product.

The decomposition of calcium sulphide by carbon dioxide has long been known, and was the subject of many experiments by Gossage and others more than fifty years ago. The great objection to the use of this method has always been the irregular composition and amount of the hydrogen sulphide liberated. In 1882 Opl proposed to pass carbon dioxide into the tank-waste suspended in water, and to conduct the hydrogen sulphide given off into fresh waste, forming calcium hydrosulphide, which could then be treated with magnesium chloride as in Schaffner and Helbig's process. In other words, Opl proposed to accomplish by carbon dioxide the same result as Krausshaar by heating with water, namely, the concentration of the sulphur of the waste and separation of half the lime.

The process introduced by Chance Bros.[1] is in some respects an extension of that of Opl, and happily overcomes the practical difficulties which opposed the early experiments of Gossage and others who sought to accomplish the decomposition of tank-waste by carbon dioxide. This process seems to furnish a complete solution of the long standing problem of sulphur recovery.

Tank-waste suspended in water is introduced into vertical cylinders, through a series of which the gases from closed lime-kilns, consisting of about 70 per cent. nitrogen and 30 per cent. carbon dioxide, are pumped under pressure. The hydrogen sulphide given off in the first tanks is absorbed by the waste in the succeeding ones, with the formation of hydrosulphide, while the inert nitrogen passes through the series and is allowed to escape. When the gas coming from one of the tanks contains a sufficient proportion of hydrosulphide (shown by burning well in a Bunsen lamp), connection is made with a large gasholder, and the gas collected and stored for use. This gas is of constant composition, contains over 30 per cent. of hydrogen sulphide, and is of suitable strength for burning to sulphur dioxide for the manufacture of sulphuric acid, or for the preparation of sulphur by the "Claus kiln," in which the hydrogen sulphide is burned with the necessary amount of air to produce water and free sulphur, according to the reaction,

$$H_2S + O = H_2O + S.$$

Mr. Chance, in the paper mentioned above, describes the working of this kiln as follows: "The process is performed by mixing sulphuretted hydrogen with a *regulated quantity* of air, and sending the mixture through a layer of anhydrous oxide of iron, which, by the heat generated by the reaction itself, is maintained at a dull red

[1] J. Soc. Chem. Ind. 1888, p. 163.

heat, the oxide of iron itself undergoing no change. Free sulphur, accompanied by the vapor of water, passes off, the sulphur being obtained in the fused or sublimed form, according to the temperature of the kiln and of the depositing chambers."

Prior to March, 1888, the firm named had recovered by the above process 90 per cent. of the sulphur from over 3000 tons of waste, and claim that the operation of obtaining hydrogen sulphide and burning it to sulphur or sulphuric acid is in every respect cheap, simple and satisfactory. No fuel is required in any part of the process. The precipitated calcium carbonate is as suitable for the black ash process as that obtained by Schaffner and Helbig's method, and its value for this purpose is increased by the fact that it contains about two per cent. of sodium salts. The sulphuric acid obtained is extremely pure and free from arsenic. It is estimated that if this process were universally adopted, at least 100,000 tons of sulphur could be annually recovered, which is nearly equal to the whole amount imported from Sicily into England and America.

It would seem that this process, with the present low price of pyrites and the prospect of still further reduction, might turn the tide in favor of the Leblanc process. That the fall in the price of pyrites which has already taken place is not in itself sufficient, is shown by the continued steady decrease in the production of Leblanc soda in England since 1883. It remains to be seen to what extent the Chance process of sulphur recovery may change for the better the position of Leblanc soda-makers.

The Parnell and Simpson Alkali and Sulphur Process.—A very interesting novelty in the alkali industry is the combined Leblanc and Ammonia process of Parnell and Simpson, which has been worked experimentally in England since 1885, and the details of which have just been published.[1] In this process sodium bicarbonate is obtained by treating brine and *ammonium sulphide* with lime-kiln gases, and the resulting ammonium chloride is reconverted into sulphide by heating with Leblanc tank-waste. The waste and ammonium chloride are heated in vats by steam:

$$CaS + 2NH_4Cl = CaCl_2 + (NH_4)_2S.$$

The ammonium sulphide distills off and is absorbed in strong brine. The carbonating operation takes place in two stages, in the first of which no hydrogen sulphide is given off and the inert gases are allowed to escape:

$$(NH_4)_2S + H_2O + CO_2 = HNH_4CO_3 + HNH_4S.$$

In the second stage, complete conversion into bicarbonate takes place, with liberation of strong hydrogen sulphide:

$$HNH_4S + CO_2 + H_2O = HNH_4CO_3 + H_2S.$$

[1] J. Soc. Chem. Ind. 1889, p. 11.

The bicarbonate reacts with the salt present, producing sodium bicarbonate; the hydrogen sulphide is partly burned to sulphur dioxide, which is made to act on the remainder of the hydrogen sulphide, producing sulphur, as in the Schaffner and Helbig process. The inventors claim to have made improvements by which the latter reaction can be successfully carried out.

This process virtually makes a modified ammonia-soda process a means of recovering the sulphur from Leblanc waste. The advantage of this combination over a Leblanc plant recovering sulphur by the Chance process, and an ordinary ammonia-soda works, would be merely in the saving of the lime needed to regenerate the ammonia in the latter process. As a new method for the recovery of sulphur from tank-waste, the Parnell and Simpson process may, however, have an important future.

The Weldon-Pechiney Process.—Meanwhile there are two important directions from which further help may come to the ammonia-soda industry, the first of which is the Weldon-Pechiney chlorine process, now being successfully worked at Salindres, in the south of France.[1] This is based upon a reaction which has long been known, the decomposition of moist magnesium oxychloride by heat, giving free chlorine and hydrochloric acid.

Magnesium chloride is obtained by dissolving magnesia in the hydrochloric acid produced in the process. The solution of the chloride is evaporated to a certain point, and an equivalent quantity of magnesia added. The mass becomes solid, is broken up into lumps and partially dried. At this stage the oxychloride contains about 25 per cent. of water. It is charged into narrow retorts intensely heated by gas. About 80 per cent. of the chlorine contained is given off, of which about one-half is free chlorine. The hydrochloric acid is condensed by water, and the chlorine used for making chlorate.

By this method hydrochloric acid may be made to yield over 80 per cent. of its chlorine in the free state, while by the Weldon process (recovering the manganese dioxide), only 33 per cent., and by the Deacon process only 40 to 50 per cent. are obtained.

The effect of this process upon the Leblanc-soda industry depends upon the fact that it may furnish a cheap source of chlorine for making bleaching powder, thus diminishing the value of the chief bye-product of the Leblanc process. The Weldon-Pechiney process is especially applicable in places where magnesium chloride is a waste product. It is estimated that if established at Stassfurt, where great quantities of waste magnesium chloride are produced, bleaching powder could be manufactured there at a cost of five pounds sterling per ton, while the present cost of production in England is thirteen pounds per ton.

Recovery of Chlorine in the Ammonia-Soda Process.—It is generally acknowledged that if the chlorine of the salt treated

[1] Dewar, J. Soc. Chem. Ind. Dec. 1887.

by the ammonia-soda process, which is now wholly lost as calcium chloride (of which more than a ton is discarded for every ton of soda-ash produced), could be cheaply recovered and made available for making bleaching powder, etc., the final supremacy of the ammonia-soda process would be assured. Many attempts to accomplish this have been made, but as yet no commercially successful process has been made public. Solvay has been engaged for years in experiments on the decomposition of calcium chloride by means of silica and clay at high temperature, while Mond asserts his full confidence in the final success of his plan of decomposing ammonium chloride into ammonia and hydrochloric acid. This is to be effected by passing ammonium chloride vapor over heated nickel oxide (or other oxides), by which hydrochloric acid is absorbed and ammonia liberated; the nickel chloride is then decomposed by highly heated steam or air, with the reformation of the oxide. Another plan is that of Twynam, who converts calcium chloride into the oxychloride by addition of lime, and then decomposes the oxychloride by heating in a current of air, exactly as the magnesium oxychloride is decomposed in the Weldon-Pechiney chlorine process. Mond has just patented a method of obtaining ammonia and chlorine from ammonium chloride,[1] which is practically an application of the Weldon-Pechiney to the ammonia-soda process. Ammonium chloride vapor is passed over heated magnesia to which 5 or 10 per cent. of sodium or potassium chloride has been added. Ammonia and steam are produced, and magnesium chloride remains. The latter is then decomposed by heating intensely in a current of air; chlorine is given off, and magnesium oxide is left behind to be again treated with ammonium chloride. No account of the practical working of these processes on a large scale has, however, been made known.

The Ammonia-Alkali Industry.—In conclusion, it may be of interest to consider briefly the present state of the alkali industry in the United States.

A small amount of Leblanc soda was formerly made in this country, but so far as is known to the writer, this industry does not exist here at present. Caustic soda has been made by the Cryolite process for many years by the Pennsylvania Salt Manufacturing Co. at their works at Natrona, near Pittsburg. This company enjoyed for a long period the right to two-thirds of the Cryolite mined at Evigtok, Greenland.

Nearly all the soda-ash used for glass and soap making in this country was until very lately imported, chiefly from England. In 1882 the Solvay Process Co. was established at Syracuse, N. Y., and soon after that time the manufacture of ammonia-soda was commenced at these works. The production rapidly increased, and in 1888 amounted to over 60,000 tons, or one-third of the total

[1] J. Soc. Chem. Ind. 1888, p. 845.

quantity of soda consumed in the United States. Caustic soda is also made by this firm on an extensive scale. Explorations undertaken by the Syracuse Company have resulted in the discovery of valuable deposits of salt, sufficient to supply the needs of the works indefinitely.

Dr. Francis Wyatt, in the articles on Chemistry Industry mentioned above, urges the adoption of the Leblanc process in this country, as best suited to the peculiar conditions which here prevail. At the time of the publication of his papers, the success of the Chance process of sulphur recovery, which is undoubtedly of great importance in this connection, had not yet been announced. It would seem that the establishment of a Leblanc plant in a suitable locality in this country, using Spanish pyrites, working the cinders for copper and silver, manufacturing bleaching powder and recovering the sulphur by Chance's process, must be successful. Over 50,000 tons of bleaching powder and 85,000 tons of Sicilian sulphur are annually imported into the United States; these products would therefore find a ready market.

The rapid development of the ammonia-soda industry at Syracuse, however, shows that that process is well adapted to the needs of the country, and it is probable that these works, or branch establishments located at other places, will, in the near future, supply the whole American demand for alkali.

SPENCER B. NEWBURY.

REPORT ON SOME RECENT ADVANCES IN PHYSIOLOGICAL CHEMISTRY.

In a volume of "Studies" recently issued from the laboratory of physiological chemistry of Yale University,[1] there are given the results of nine investigations relating to subjects of more or less importance in physiological chemistry. Of these, three deal with the primary cleavage products formed from elastin, casein and myosin by the action of the proteolytic ferments pepsin and trypsin, and also by the hydrolytic action of boiling dilute acid.

On heating moist elastin with water containing a trace of hydrochloric acid for some hours at or near 100° C., it was found that the elastin soon commences to swell, and after a time is converted into a semi-gelatinous mass, a portion of which, as the heating is continued, becomes soluble and passes into the acid fluid. The liquid gives no reaction with tannic acid for gelatin, but does give a strong biuret reaction, and with an excess of caustic alkali shows a heavy turbidity. The soluble matter consists of two distinct bodies called respectively proto- and deutero-elastose, which bear the same relation to elastin that the corresponding albumoses[2] do

[1] Studies from the laboratory of physiological chemistry, Sheffield Scientific School of Yale University, Vol. III, edited by R. H. Chittenden, Ph. D., professor of physiological chemistry. New Haven, January, 1889.

[2] See this Journal **6**, 31 and 101.

to albumin. Further, like the albumoses, they are completely precipitated from a neutral fluid by saturation with ammonium sulphate. Proto-elastose is precipitated by saturation of a neutral fluid with sodium chloride, while deutero-elastose is precipitated from a salt-saturated solution by addition of dilute acetic acid. Proto-elastose is readily soluble in cold water, but only slightly in hot water. In a neutral solution, heat produces a turbidity or coagulum which disappears as the fluid cools. Long-continued evaporation of an aqueous solution of proto-elastose leads to a separation of more or less of the substance as a gummy mass. Concentrated mineral acids produce precipitates soluble in excess of acid. Alcohol partially precipitates the substance, and phosphotungstic and picric acid both produce precipitates. The elastose is but slightly, if at all, diffusible, and in composition does not differ essentially from the original elastin. Deutero-elastose, on the other hand, contains a smaller percentage of carbon than elastin, and further differs from proto-elastose in that it is completely soluble in hot and cold water, and is not precipitated by the mineral acids, by alcohol, nor by acetic acid and potassium ferrocyanide. It is also more readily diffusible.

By the action of pepsin-hydrochloric acid at the body temperature, powdered elastin was found quite easily digestible,[1] and although apparently no true peptones were formed (*i. e.* soluble products not precipitated by saturation with ammonium sulphate), large amounts of proto- and deutero-elastose were obtained similar in reactions to those already described. Bodies of like nature, but of somewhat different composition, were also formed by digestion of pure elastin with an alkaline solution of trypsin.

The composition of the several elastoses and their relation to elastin is shown in the following table:

	Elastin *A.*	Elastin *B.*	Action of acid water at 100° C.		Action of pepsin-hydrochloric acid.		Action of alkaline trypsin solution.	
			Protoelastose.	Deutero-elastose.	Protoelastose.	Deutero-elastose.	Protoelastose.	Deutero-elastose.
C	54.24	54.08	54.27	53.26	54.52	53.11	53.05	54.65
H	7.27	7.20	7.12	7.12	7.01	7.08	7.02	7.04
N	16.70	16.85	17.02	16.70	16.96	16.85	16.88	16.55
S	..	0.30	..	..	..	..	..	..
O	21.79	21.57	21.59	22.92	21.51	22.96	23.05	21.76
Ash	0.90	0.31	1.47	2.01	1.34	5.02	7.38	5.45

Casein, on being subjected to the action of artificial gastric juice, is decomposed into soluble caseoses and peptone, but in every digestion there invariably remains a certain amount of an insoluble,

[1] Compare Horbaczewski, Ztschr. physiol. Chem. **6**, 330.

pasty, grayish-white substance, which is not susceptible to the action of pepsin-acid, no matter how long continued. This insoluble substance, noticeable to a greater or less extent in the pepsin digestion of all proteids, but particularly so with casein, was named casein-dyspeptone by Meissner, and later, in 1870, was fully described by Lubavin,[1] who looked upon it as a mixture of two bodies, one of which was considered as containing 4.6 per cent. of phosphorus and having the formula $C_{21}H_{46}N_6PO_{11}$. A careful study of this dyspeptone, prepared from pure casein by a large number of separate digestions with pepsin-hydrochloric acid, has resulted in showing that this substance is a mixture of calcium phosphate with a hydration-product of casein, the hydrochloric acid compound of which is insoluble in water and dilute acid. The so-called dyspeptone, when freed from acid, is quite readily soluble in water, the solution remaining unchanged on boiling. It is precipitated by saturation of its aqueous solution with ammonium sulphate, but not by sodium chloride. Addition of acetic acid to the salt-saturated fluid gives the usual precipitate of dyspeptone. Acetic acid, when added to an aqueous solution of the substance, gives a heavy white precipitate, insoluble in moderate excess of acid, but entirely soluble in a large excess on application of heat. Addition of potassium ferrocyanide to the clear acid fluid gives only a faint turbidity.

The following table shows the average composition of the several dyspeptones studied:

	A.	B.	C.	D.	E.	F.	G.	Casein.
C	51.15	51.07	51.29	51.82	50.80	51.60	50.39	53.30
H	7.18	7.41	7.26	7.44	6.73	6.83	6.63	7.07
N	15.16	15.41	15.23	15.48	15.12	15.19	15.58	15.91
S	0.71	0.71	0.68	0.78	...	...	...	0.82
P	0	0	0	0	...	...	...	0.87
O	25.80	25.40	25.54	24.48	...	...	...	22.03
Ash	13.67	15.41	12.43	14.19	14.96	13.60	12.71	0.98

The ash was composed almost entirely of calcium phosphate, and the dyspeptones apparently contained no phosphorus whatever, other than that combined with calcium.

In the digestion of casein with pepsin-acid, the relative proportion of individual caseoses formed was found to depend somewhat upon the strength of the pepsin solution and the length of time the ferment was allowed to act. All of the caseoses are precipitable by saturation with ammonium sulphate. Proto-caseose, like the corresponding albumose, is precipitated from an aqueous solution by addition of rock-salt to saturation. Dry proto-caseose when moistened with water becomes immediately gummy and soon dissolves to a perfectly clear fluid, which on addition of considerable water becomes decidedly turbid. Treated with a large amount of water at the outset, it dissolves more slowly, giving

[1] Hoppe-Seyler's Med. chem. Untersuchungen, p. 463.

a more or less cloudy fluid. In dilute acids and in dilute sodium carbonate it dissolves to a perfectly clear fluid. Towards heat, aqueous solutions of proto-caseose act exactly like proto-elastose. Even when warmed very gently, the solution becomes quickly turbid, and if concentrated, gives more or less of a precipitate. On cooling, the turbidity disappears, reappearing as the fluid is heated. Like proto-elastose also, a solution of the caseose body, on being rapidly concentrated, deposits more or less of the substance as a gummy mass, which, however, dissolves in cold water, or if the fluid is not too concentrated, dissolves in the mother-liquor as it cools.

Two forms of deutero-caseose were obtained, called respectively α and β deutero-caseose. Both of these bodies stand much nearer to true peptone than proto-caseose, β-deutero especially so. α-deutero-caseose is partially precipitated from a salt-saturated fluid by a little acetic acid, and completely by saturation with ammonium sulphate in the cold; while β-deutero is precipitated as a sticky gum by ammonium sulphate, on boiling a solution saturated with the salt. The latter substance is especially characterised by a low content of carbon, and by its non-precipitation with acetic acid and potassium ferrocyanide, with nitric acid and with cupric sulphate. It stands unquestionably nearer to peptone than α-deutero, and is doubtless formed from the latter by the continued action of the ferment. α-deutero differs in its reactions from proto-caseose, especially in that it is quickly and completely soluble in water, and the solution when heated gives no coagulum whatever; also, in not giving any precipitate with either acetic or nitric acid. Bodies called hetero-caseose and dys-caseose were also formed, which resembled in many ways the corresponding albumoses. Further, by the action of dilute sulphuric acid at 100° C., and also by the action of the pancreatic ferment trypsin, caseoses of the same general nature as the preceding were formed.

On supersaturation of a digestive fluid with ammonium sulphate at 100° C., all of the preliminary products of proteolytic action are entirely removed, and in the present state of knowledge we assume as peptone any amorphous product of proteolytic action precipitable by alcohol and not precipitable by heating with ammonium sulphate added to saturation. With this fact in mind, casein antipeptone was formed by long-continued digestion of pure casein with alkaline solutions of trypsin, and then freed from all adhering proteoses. The purified peptones were found to be exceedingly gummy and excessively hygroscopic, requiring long-continued drying at 110° C. to remove the last traces of moisture. In reactions, they are characterised by extreme solubility in water, non-precipitation by nitric or acetic acid, by acetic acid and potassium ferrocyanide, by cupric sulphate, and by saturation with ammonium sulphate both in neutral and acid solutions. During the drying of the peptones at 110° C., prior to analysis, they apparently under-

went a slight decomposition, indicated by the odor of valerianic acid; and likewise appeared to undergo a partial retrogressive metamorphism, inasmuch as after the drying, the preparations gave noticeable precipitates with nitric and acetic acids, and also by saturation with ammonium sulphate.

The composition of the casein antipeptones, and also of some of the caseoses, is shown in the following table:

		By Pepsin-acid.			By Trypsin.				
							Antipeptone.		
	Casein.	Proto-caseose.	α-deutero-caseose.	β-deutero-caseose.	α-deutero-caseose.	β-deutero-caseose.	A.	B.	C.
C	53.30	54.58	52.30	47.72	56.17	53.56	49.94	51.38	49.52
H	7.07	7.10	6.95	6.73	6.90	6.70	6.51	6.47	6.60
N	15.91	15.80	16.40	15.97	14.80	15.07	16.30	15.57	15.99
S	0.82	...	...	...	...	0.93	0.68	...	...

The researches of Kühne,[1] Hoppe-Seyler,[2] Weyl,[3] and Danilewsky[4] have shown that myosin, both from the animal and vegetable kingdom, is a globulin body, soluble in dilute sodium and ammonium chloride solutions, and precipitable therefrom either by the addition of salt in substance, or by dilution with much water. In spite of the interest attached to this peculiar proteid, little attention has been paid to its chemical nature since the time of its discovery by Kühne, and no attempt has hitherto been made to ascertain either its composition or whether the myosin obtainable from different animal sources is of the same chemical nature. Myosin was therefore prepared by extraction of thoroughly washed muscle-tissue from various sources, with either sodium or ammonium chloride solution (5–15 per cent.), and precipitation either by dilution with water or by dialysis until the salt was entirely removed. A large number of preparations were studied, thirteen of which were analysed, from ox, calf, sheep, fish, and other muscle, and showing such a close agreement that it is obvious that myosin as it occurs throughout the animal kingdom is a single chemical compound of constant composition. The average composition of all the preparations was as follows:

C 52.82, H 7.11, N 16.77, S 1.27, O 21.90,

being almost identical with the figures found by Hammarsten[5] for fibrinogen.

The coagulation point of an ammonium chloride solution of myosin was found to average about eleven degrees lower than a sodium chloride solution of the same strength, while a 5 per cent. sodium chloride extract of ox and sheep muscle grew turbid at about 57° C., and gave a flocculent precipitate at 63° C. Corresponding extracts of rabbit's, lamb's, calf's, and chicken muscle grew turbid at 52°–53° C., and gave a flocculent precipitate at 57°–62°

[1] Protoplasma, Leipzig, 1864; also Lehrbuch der physiologische Chemie, 4 Auflage, p. 236. [2] Handbuch der chem. Analyse. [3] Ztschr. physiol. Chem. Band **1**, p. 72. [4] Ibid, Band **5**, p 158.

[5] Jahresbericht der Thierchemie **10**, 11.

C. The results collectively fail to show the presence of a proteid coagulating at 47° C., given by Halliburton[1] as characteristic of myosin; but they do show a coagulum at about 56° C., corresponding to Halliburton's second proteid. Coagulums were also obtained at higher temperatures, showing an approach, at least, to the figures found by Halliburton in his fractional coagulation of salted muscle-plasma. Doubtless, myosin is formed, as suggested by Halliburton, by the interaction of one or more myosinogens and a ferment body.

Pure myosin was also digested with a solution of pepsin-hydrochloric acid, and its primary cleavage products studied and analysed. Proto and deuteromyosinose were obtained in considerable quantity; hetero and dysmyosinose only in small amount. The reactions of protomyosinose agree in general with those of protoalbumose, but with one important difference, viz., that an aqueous solution of the former free from salt, of whatever concentration, is not rendered turbid by nitric acid. Concentrated solution of sodium hydroxide, as in proto-elastose, produces a heavy, flocculent, gelatinous precipitate. Both proto and deuteromyosinose in aqueous solution react alkaline. In general, deuteromyosinose shows much the same reactions as the corresponding albumose, but is somewhat different from the latter, in that it is more difficultly precipitable. In composition, protomyosinose does not differ essentially from myosin, while deuteromyosinose contains a somewhat smaller percentage of carbon.

	C.	H.	N.	S.	O.
Myosin,	52.79	7.12	16.86	1.26	21.97
Protomyosinose,	52.43	7.17	16.92	1.32	22.16
Deuteromyosinose,	50.97	7.42	17.00	1.22	23.39

Myosin was found difficultly digestible in gastric juice, and the somewhat large residue of unaltered myosin was warmed for some days with a strong solution of trypsin, but still a large residue remained undissolved. The portion digested by the trypsin was found mainly as peptone, no myosinoses apparently being present.

Experiments on the physiological action of uranium salts are also recorded, as likewise the results of experiments on the influence of urethan, paraldehyde, antipyrin, and antifebrin on proteid metabolism. Uranium nitrate, from experiments on a large number of animals, is shown to be an irritant poison, producing gastro-intestinal irritation of more or less intensity. It is not in any sense a rapid poison, and the ingestion of a fatal dose of a uranium salt is not followed by any noticeable effect for some time; further, the action of a small amount (150 milligrams) is apparently as rapid and pronounced as that of large quantities (1 gram). The first noticeable symptom in rabbits is general weakness, lack of motor power, loss of co-ordination, and occa-

[1] Journal of Physiology **8**, 133.

sional temporary paralysis of the locomotor muscles. Introduced into the stomach in sufficient amounts, it checks digestion, and even stops it altogether. On the other hand, it appears to increase somewhat proteid metabolism, and also to increase the elimination of carbonic acid, and to raise the body temperature. Hence it is to be considered as having a direct action on nutrition, the disturbance of which is also plainly indicated by the rapid emaciation which follows the administration of uranium. It has a marked destructive action on the kidneys, causing an acute parenchymatous nephritis of the same kind as found in arsenic, mercury and phosphorus poisoning. Further, the large quantity of albumin found in the urine shows plainly that the blood-vessels are seriously involved in the inflammation. The albuminuria produced is severe and constant, and when the uranium is given in a single large dose, or in a small dose by hypodermic injection, albumin may appear in the urine within twenty-four hours. With small doses of uranium, the urine is decidedly increased in volume; but later on, when toxic action is more pronounced, there may be a partial or even complete suppression of the urine. The urine, too, in a short time after the administration of uranium, contains more or less sugar, but as a rule the sugar does not make its appearance until after the albumin. In the hypodermic injection of uranium, sugar appeared in a rabbit's urine within twenty-four hours. The production of glycosuria was found to be quite a characteristic symptom of uranium poisoning.

The influence of ethyl-urethan, antipyrin, and antifebrin on proteid metabolism, was studied by experiments upon healthy men, brought into a condition of nitrogenous equilibrium and fed upon a weighed diet of known composition throughout the experiment, which in each case extended over a month. The action of paraldehyde was studied in a similar way upon a large coach dog. The urine was analysed each day; in two of the experiments, total nitrogen, sulphur, and phosphorus were determined, while in the the other two, urea, uric acid, phosphoric acid, and chlorine were estimated.

The results obtained indicate that antipyrin has a decided inhibitory influence on the proteid metabolism of the healthy human organism, as shown by the diminished excretion of urea and uric acid when the drug was taken. Also, that antipyrin tends to diminish the volume of the urinary secretion. These conclusions are contrary to the recent results published by Kumagawa,[1] who found by experiments on a dog that antipyrin produced no change in the excretion of nitrogen, but did cause a noticeable increase in the excretion of uric acid.

Antifebrin or acetanilide in doses sufficiently large to produce an approach to cyanosis (214 grains in 7 days), gave rise to a slight increase in the excretion of urea; but as there was no

[1] Virchow's Archiv, Band **113**, 192.

corresponding increase in the excretion of either sulphur or phosphorus, it was not considered as having any very pronounced influence on proteid metabolism. On the excretion of uric acid, however, it appeared to exercise a special inhibitory influence.

Urethan was found to have a very decided diuretic action, and even in small doses greatly diminished the excretion of nitrogen. The excretion of sulphur was correspondingly diminished, but with small doses the excretion of phosphorus was apparently increased.

Paraldehyde, in the quantities given, had no special action on the excretion of either nitrogen, sulphur or phosphorus. Further, paraldehyde was found to increase somewhat the proteolytic action of pepsin-hydrochloric acid, but to have a very pronounced inhibitory influence on the amylolytic ferment of saliva. Antifebrin, even in very small quantities, checks the solvent power of saliva on starch, and also retards the action of pepsin. Antipyrin has only a very slight effect on the salivary ptyalin, but checks the action of pepsin; while urethan increases the amylolytic action of saliva, and retards only slightly the proteolytic action of pepsin.

Finally, we have space only to mention the experiments tried upon rabbits with soluble nickel and cobalt salts, with a view to studying the distribution of the absorbed poisons and their relative toxic action. The results collectively show that the two salts act very much alike, and that their poisonous action is somewhat slow, and manifested only when comparatively large amounts of the salts are administered. Both apparently cause death by stopping the action of the heart,[1] and also produce more or less disturbance in the alimentary tract, interfering with digestion, producing more or less inflammation of the mucous membrane of the stomach and intestine, and causing a more or less persistent diarrhœa. Both salts tend to produce a partial paralysis of the extremities, more pronounced possibly with cobalt than with nickel. They enter the circulation quickly, are rapidly distributed to all parts of the body, and are in turn more or less rapidly eliminated by the kidneys. Considerable, however, passes directly through the alimentary tract and is excreted with the faeces. The storage power of the individual organs is somewhat peculiar. The spinal cord and brain, in the majority of the experiments, stand first in their power of picking up and retaining the absorbed nickel and cobalt. This is in close accord with what has already been found with soluble forms of arsenic,[2] and more recently with strychnine[3] sulphate. Again, as with soluble forms of arsenic, the muscle-tissue retains a larger percentage of the metals than either the liver or kidneys. Another noticeable feature in the distribution of the absorbed poison is the comparatively large amounts retained by the lungs and heart.

[1] See Blake, Amer. Jour. Science and Arts **7**, 194.
[2] This Journal **5**, 8, 12. [3] Journal of Physiology **9**, 99.

Blair's Chemical Analysis of Iron.[1]

The term "technical analysis," as generally used, implies a short method which gives results of sufficient accuracy to serve as a guide in controlling a manufacturing operation. When, however, the chemical analysis is the basis on which ores or products are bought and sold, the most exacting demands are made on the chemist for the highest attainable accuracy.

From this standpoint, it is very interesting to follow the literature of the chemical analysis of iron for the last twenty-five years. The manufacture of steel by the Bessemer process had its foundation on the chemical determination of minute amounts of phosphorus in irons and iron ores; and the development to its present colossal proportions has only been made possible by the patient and exhaustive investigation of the composition of steel of different physical properties. But the steel-maker has not been content with mere accuracy. Owing to the great rapidity with which, in a modern steel plant, pig-iron is converted into steel ingots and these ingots into rails, the chemist has been compelled to devise shorter processes in order to keep pace with the work in the mill, and the result has been that there have been perfected in the chemical laboratories of iron and steel works methods which are marvels of rapidity and accuracy.

A book which should bring together an account of the principal modern methods for the chemical analysis of iron ores, pig-iron, steel, and the materials used in iron and steel making, has long been needed. Troilius's *Notes on the Chemistry of Iron* is excellent as far as it goes, but its scope is limited. Jüptner von Jornstorff's *Praktisches Handbuch für Eisenhütten-Chemiker* is probably the best book devoted entirely to this subject, but it is not accessible to chemists without a knowledge of German. It will be, without doubt, generally admitted that the person best qualified in this country to write a book on chemical methods of iron analysis is Mr. Blair. His long experience in work of this kind, both in his private practice and as chemist of the United States Board appointed to test iron, steel and other metals in 1875, and of the United States Geological Survey, and the Tenth Census, has made him the first authority on this subject. It is therefore a matter of congratulation for all chemists that Mr. Blair has taken the time from a busy professional life to write a work which might otherwise have been undertaken by a less competent hand.

The compilation of the best methods now in use has been well done, and, in some cases, Mr. Blair has had contributions prepared specially for this book, from chemists of steel works, describing their own methods. But the great value of the book will be found,

[1] The Chemical Analysis of Iron: A complete account of all the best known methods for the analysis of iron, steel, pig-iron, iron ore, limestone, slag, clay, sand, coal, coke, and furnace and producer gases. By Andrew Alexander Blair. Philadelphia: J. B. Lippincott Company, 1888.

we think, in the detailed description of processes as carried out by Mr. Blair in his own practice. Uniformity of treatment and manipulation is necessary often to ensure agreeing results; the mere outline of a process will often mislead. The patience with which Mr. Blair has, in many cases, given each step of the process as he performs it, is much to be commended.

We could wish that Mr. Blair, in describing various methods for the determination of the same element, had permitted himself the privilege of criticism and comparison of the methods as regards accuracy and simplicity of working. A beginner who goes to the book to find the best method for determining a certain element may find himself embarrassed by the choice presented to him. This is notably the case in regard to carbon. All the processes which have ever been proposed for the determination of total carbon in iron are here admirably classified, but the reader is not informed that some of these processes have fallen into disuse either because inaccurate or because there are simpler ones available.

In the chapter on the determination of metallic iron in iron ores there is a singular omission to mention the use of mercuric chloride to convert into stannic chloride any excess of stannous chloride which may have been used in the reduction of the ferric chloride. This is by far the simplest and most perfect of all the methods in use for the reduction of ferric salts previous to titration. It has long been in use for the bichromate method, and has recently been adapted to the use of permanganate, by the addition of manganous sulphate to the solution. Pulverised zinc should also have had mention as a more convenient agent for reducing ferric solutions than granulated zinc.

In fusions with alkaline carbonates and nitre for the determination of sulphur, Mr. Blair implies that the only danger of the sulphur in the gas being absorbed by the fusing mixture is when the mass overflows the outside of the crucible. We think most chemists will not agree with him on this point. An appreciable absorption of sulphur from the gas by the fused mass in the crucible has been noted when the fusion lasts fifteen minutes or more. Fusion in a gas muffle is accompanied by much less contamination with sulphur than when the crucible is heated over the free flame, but an alcohol lamp is, in all cases, to be preferred for fusions for sulphur. The apparatus described in the book, many of which are original with Mr. Blair, are characterised by fitness and simplicity, and the cuts of them are models of clearness. The book is also to be praised for admirable typography and good paper. But we cannot help thinking that the fair page is marred by the general use of chemical symbols for abbreviations. This practice is objectionable from any point of view, and we cannot think why the author adopted it, unless it was to save space. For our part we should have preferred the book in greater bulk rather than to read "HCl" in place of "hydrochloric acid."

In connection with the thorough modern character of the book as regards methods, it is interesting to observe the conservatism of the author in clinging to the older nomenclature. "Acetate of sodium and carbonate of calcium" look strangely in a modern chemical book. Occasionally the author is off his guard and there slips in the more recent form, giving a rather droll effect, as when "cupric chloride" and "sulphate of copper" stand side by side. But these are not serious blemishes.

The table of atomic weights is not fully abreast of the latest research, and might be advantageously revised in a future edition.

Mr. Blair says, in his preface, that the work "is intended to be a guide for the student of iron chemistry only." The book is sure of a warm welcome from the chemists of iron works, but, if we mistake not, it will have an equally cordial reception from teachers of chemistry, many of whom lack an intimate knowledge of the chemical practice of iron and steel works.

T. M. DROWN.

NOTES.

A New Technical Method of Preparation and a Partial Synthesis of Cocaine.

The cocaine extracted from coca leaves contains a number of other alkaloids from which it must be separated. These alkaloids have hitherto been of no value, and their presence has only interfered with the preparation of cocaine. C. Liebermann and F. Giesel[1] have recently shown that by boiling the alkaloids for an hour with hydrochloric acid they are all converted into ecgonine. They have further succeeded in devising a method for converting ecgonine into the benzoyl derivative, and benzoyl-ecgonine can, finally, be converted into methyl-benzoyl-ecgonine or cocaine by the method of Einhorn. The preparation of benzoyl-ecgonine is effected by digesting ecgonine, water, and benzoic anhydride on a water-bath. It is thus possible to convert a very considerable quantity of otherwise worthless compounds into the valuable cocaine.

I. R.

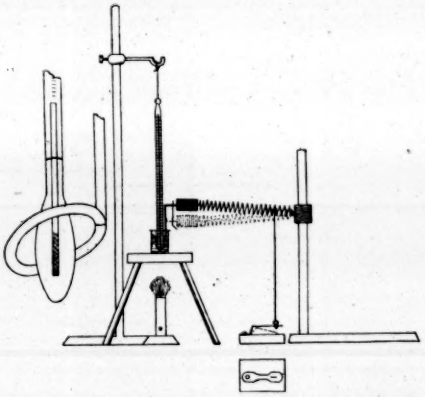
An Attachment for Stirrers Used in Determining Melting Points.

To obviate the ordinary difficulties met with in stirring the liquid of the bath used in determining melting points, the apparatus described below has been devised. The attachment for the stirrer consists of a spiral about eight inches long and three-

[1] Ber. d. chem. Gesell. **21**, 3196.

eighths of an inch in diameter, made by coiling a wire around a glass rod or tube.

The wire should be stiff enough to support a small glass stirrer at one end, and yet not so stiff as to prevent it from oscillating readily when gently touched. At one end of the spiral the wire is coiled around a small cork, which is perforated to receive the handle of the small glass stirrer. The other end of the spiral is firmly attached to a larger cork, which is perforated so as to fit tightly the upright rod of a lamp-stand. A spring about two and three-quarter inches long, made from a thin strip of brass by cutting and bending to the form shown in the figure, is screwed to a small wooden block. About half an inch from the free end is soldered a small hook made of copper wire. This hook is connected by means of a light wire with the spiral above.



In setting up the apparatus, the cork should be arranged on the lamp-stand so as to bring the loop of the stirrer just under the surface of the liquid in the beaker when the spring is at rest. The press-spring should be as light as practicable, so as to offer the minimum resistance, and the block carrying it should be weighted or screwed to the desk, to avoid displacement while stirring.

If the wire connecting the hook with the spiral is attached to the latter two inches from the fixed end, when the press-spring is moved downward a quarter of an inch by means of the forefinger, the stirrer will have a one-inch stroke. On removing the finger, the spiral spring carries the stirrer back to the original position. By the use of this apparatus the temperature of the liquid is kept

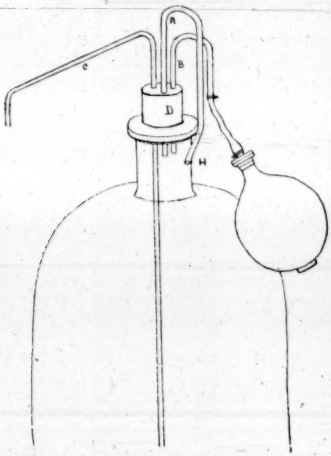
uniform, and the investigator is enabled to put the whole of his attention on the thermometer and the substance being melted, while his forefinger operates the stirrer without becoming wearied.

EDWARD C. HOLTON.

MASS. INST. TECH., BOSTON, *March*, 1888.

A Simple Acid-Pump.

Although this device, in slightly different forms, has been in use for some time, yet the convenience of the modification here figured may render it worthy of description.



A, *B* and *C* are three glass tubes passing through the rubber stopper *D*, *A* and *B* ending just below the stopper, and *C* reaching to the bottom of the bottle. To *B* is attached a double-valve rubber bulb. *A* is so bent that, while the bulb is clasped in the hand, the thumb can easily be held over the open end of *A* at *H*. Acid can then be forced out through *C*, and the flow may be checked instantly by removing the thumb from *H*. The left hand is thus left free to hold under *C* the vessel into which the acid is to flow. A glazed earthenware dish is placed upon the table under *C* to catch the drippings.

For the use of large classes of beginners in general chemistry this apparatus is well adapted, since accidents resulting from careless handling are rendered almost impossible, and both acid and time are economised.

The same device may be used for carboys, the tube *C* being extended upwards so that an acid bottle may stand on the box beneath it, and *H* being kept closed by a piece of rubber tubing and a pinch-cock.

L. M. DENNIS.

CHEMICAL LABORATORY, CORNELL UNIVERSITY.